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THERMIONIC TEMPERATURE TRANSDUCER

WALTER OPPEN

FORD INSTRUMENT COMPANY
DIVISION OF SPERRY RAND CORPORATION

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FOREWORD

This report was prepared by the Ford Instrument Company, Long Island City, New York, Division of Sperry Rand Corporation, under Air Force Contract 33(615)-2445 Task Number 822404 of Project Number 8224 Exploratory Development of Thermionic Emission Techniques for Transduction of Elevated Temperatures. The work was administered under the direction of the Air Force Flight Dynamics Laboratory, Research and Technology Division, Wright-Patterson Air Force Base, Ohio, with Mr. J.V. Roberts acting as project moritor.

The report covers work performed during the period April 12, 1965 to May 13, 1966. The manuscript was released by the author for publication as an RTD technical report in September 1966.

Publication of this report does not constitute Air Force approval of the report's findings or conclusions. It is published only for the exchange and stimulation of ideas.

ABSTRACT

The purpose of this program was to prove the feasibility of using thermionic emission techniques for the transduction of elevated temperatures (above 2000° F). Several techniques were investigated, as were possible emitter materials and corrosion resistant coatings. Three transducer designs were developed. The range over which tungsten, the most satisfactory emitter material, could be expected to exhibit repeatable temperature indications was beyond the long-lifetime capabilities of the corrosion-resistant coatings. Since the designs developed were also marginal as temperature transducers, the recommendation was made that the program be terminated at the end of the study phase. Construction of the temperature transducers would not advance the state of the art of high temperature measurement. The program did not consider the suitability of thermionic techniques at temperatures under 2000° F.

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SECTION I

INTRODUCTION

The objective of the investigation reported on herein has been to determine whether the state of the art relative to the measurement and transduction of elevated temperatures can be extended through the use of thermionic emission phenomena, and to build transducers that will demonstrate that such an extension of the state of the art would permit production of transducers suitable for use in the propulsion systems, leading edges, and control surfaces of re-entry vehicles. It has been assumed for the purpose of this investigation that the state of the art below 2000° F (approximately 1400° K) is satisfactory, and that the transducers built should be capable of operation above this temperature and should extend the state of the art by exhibiting longer life, higher accuracy, or faster response above 2000° F than do existing transducers such as thermocouples and resistance thermometers. Since the objective of the study was to extend the state of the art of high temperature measurement rather than to show that temperatures capable of being measured by existing techniques can also be measured by thermionic techniques, materials and designs applicable to low temperature measurements only have not been considered.

The temperature-limited emission, also called the saturation current, from a thermionic diode is a rapidly varying function of temperature. An increase of only 100° K will in general cause at least a tenfold increase in emission current; hence, transducers based on this phenomenon should provide an extremely sensitive means of measuring small changes in temperature.

The accuracy of such a transducer is dependent on a thermionic constant known as the work function, which varies with the emitter material. Small amounts of contaminants on the surface of an emitter, or even a change in its crystalline structure, will generally alter the work function and cause large changes in the thermionic current. Considerable effort was therefore expended in considering thermionic temperature-measurement techniques that are independent of work function.

Materials for use in a thermionic temperature transducer must possess the usual requirements of high strength and corrosion resistance at elevated temperature, as well as other characteristics generally peculiar to a thermionic device, such as freedom from permeation of gases and migration of protective coatings through the substrate. These requirements, as well as the requirement that the substrate material be suitable for use as a thermionic emitter, greatly limit the choice of possible materials.

SECTION II

SUMMARY

An investigation into thermionic emission phenomena showed that high temperature operation (2000°K and above) of a tungsten emitter should result in a thermionic current that would be a repeatable function of temperature. At lower temperatures, a tungsten emitter is poisoned by residual gases and the thermionic current is then a function of the past temperature history of the emitter. However, above 2000°K the existing corrosion-resisting coatings have a lifetime of only a few hours (typically ten at 2100°K): hence, there is little possibility of constructing a long-life (100-hour) thermionic temperature transducer at the present time.

Thermionic phenomena that theoretically should produce a temperature indication independent of the emitter work function and therefore be unaffected by emitter poisoning were investigated to an extent that showed these phenomena to be small perturbations on the thermionic emission current, and of low temperature-indicating accuracy. They gave little promise of being useful in the construction of an accurate temperature transducer.

Tungsten showed the most promise as an emitter material. Of all the refractory metals investigated, it exhibited the greatest mechanical strength and the greatest freedom from poisoning. However, state of the art for refractory-metal corrosion-resistant coatings leaves much to be desired; their lifetimes at 2000°K are of the order of 12 hours and decrease rapidly with increasing temperature.

An inherent characteristic of thermionic temperature transducers is the withdrawal of large quantities of heat from the source whose temperature is being measured. The metal ceramic seals that insulate the emitter from the collector must operate at a temperature well below that of the emitter, so that heat will flow along the emitter shell to the cooler seal area. Only under conditions of excellent heat transfer from the source to the transducer can accurate temperature measurements be expected. The transducers are also inherently fragile since both emitter and collector must be heated well above the recrystallization temperature to achieve satisfactory outgassing.

An interim technical report was submitted at the end of Phase I recommending the construction of gas temperature transducers.

Subsequent to the preparation of the interim report, the error analysis was re-examined and extended to include effects which had previously been neglected. These included the effect of collector temperature on the indicated readout and the temperature-dependence of emitter poisoning. The extended error analysis showed that there was little or no hope of building an accurate temperature transducer for use between 1500° and 2000°K. Repeatable temperature indications might be obtained above 2000°K but at this temperature the corrosion-resistant coatings currently available have a short life.

It was concluded, by the contractor, that the state of the art of high-temperature measurement would not be advanced by construction of breadboard models that would be limited to operation in a high vacuum. Therefore, it was

recommended that Phase II of the project (the building of experimental breadboard models of temperature transducers designed in Phase I), be terminated. Concurrence in this recommendation by the project officer was received prior to the start of any construction.

SECTION III

BASIC CONCEPT STUDY

An initial study of the basic thermionic phenomena was undertaken to select for more detailed investigation any concepts that showed reasonable possibilities of being suitable for use in a thermionic temperature transducer. The following concepts were investigated:

Temperature-limited emission current
Diode operation in a retarding field
Diode operation in an accelerating field
Noise power development in a diode
Diode operation in a cesium vapor atmosphere.

1. TEMPERATURE-LIMITED EMISSION CURRENT

The temperature-limited emission current is the basic physical phenomenon usually associated with a thermionic diode. It is a rapidly varying function of temperature, typically changing by 10% to 25% for a 1% change in temperature. It should therefore be an extremely sensitive indicator of temperature if stable calibration of the transducer can be obtained.

The temperature-limited emission current I_s from a diode may be calculated from Richardson's equation.

$$I_s = AT^2 \epsilon^{-\phi/kT}$$

where

A = constant = (theoretically) 120 amps/(°K)^2 cm^2
T = emitter temperature in °K
ϕ = emitter work function in eV
k = Boltzman's constant 0.861×10^{-4} eV/°K.

At the same time, sufficient accelerating voltage must be applied to the diode to pull the electrons away from the emitter as fast as they escape. The necessary voltage V may be computed to a first approximation from the Child-Langmuir space-charge law for plane parallel electrodes. (Reference 1.)

$$I_s = \frac{2.335 \times 10^{-6} V^{3/2}}{X^2}$$

or

$$V = 5.65 \times 10^{3} I_s^{2/3} X^{4/3}$$

where X is the collector-emitter spacing in centimeters

At high current densities, considerable power must be dissipated in the diode. This appears in the form of heat at the collector. Figure 1 shows the voltage necessary to overcome space charge as a function of electrode spacing and emitter current. The same chart shows lines of constant collector power. A temperature scale for a tungsten emitter is shown on the abscissa for convenience.

This chart shows that at 2500°K, the collector dissipation will be about 30 watts per square centimeter for a spacing of 0.040 inches. This is close to the upper limit for collector dissipation. (It may be of interest to note that for a tungsten emitter at 3000°K, the collector dissipation would be over 20,000 watts per square centimeter. A heat flux of this magnitude will produce a temperature gradient of 5000°K/cm in copper.)

Thus, an upper limit of about 2500°K must be placed on a sensor based on the temperature-limited emission phenomenon and using a tungsten emitter. The lower limit will be around 1500°K where the thermionic current is only 10^{-7} amperes per square centimeter for tungsten, and laboratory techniques must be used for accurate measurement.

Maintenance of stable calibration is directly dependent on the maintenance of a stable emitter work function. Variation of the emitter work function with time and temperature is a serious problem in the design of a thermionic temperature transducer. Contamination of the emitter surface can and usually does cause large changes in the effective work function. Also serious is any change in the chemical composition or even any change in the crystalline structure of the surface. Since the thermionic work function is susceptible to change from many causes, it would appear difficult from purely theoretical considerations to obtain a stable work function under normal operating conditions. However, available experimental evidence shows that polycrystalline tungsten may exhibit a work function stable with time and temperature after it has been properly aged. These effects are discussed in detail in Section V.

2. DIODE OPERATION IN A RETARDING FIELD

a. Graphical Determination of Emitter Temperature. Nottingham (Reference 2) has shown that a thermionic diode operating under an externally applied retarding voltage will deliver a current I in accordance with the following formula:

$$I = AT^2 \epsilon^{\frac{-\phi_2 - V_o}{kT}}$$

where

A = constant = 120 amps/(°K)^2 cm^2
T = emitter temperature in °K
k = Boltzman's constant 0.8616×10^{-4} eV/°K
ϕ_2 = collector work function
V_o = externally applied retarding voltage.

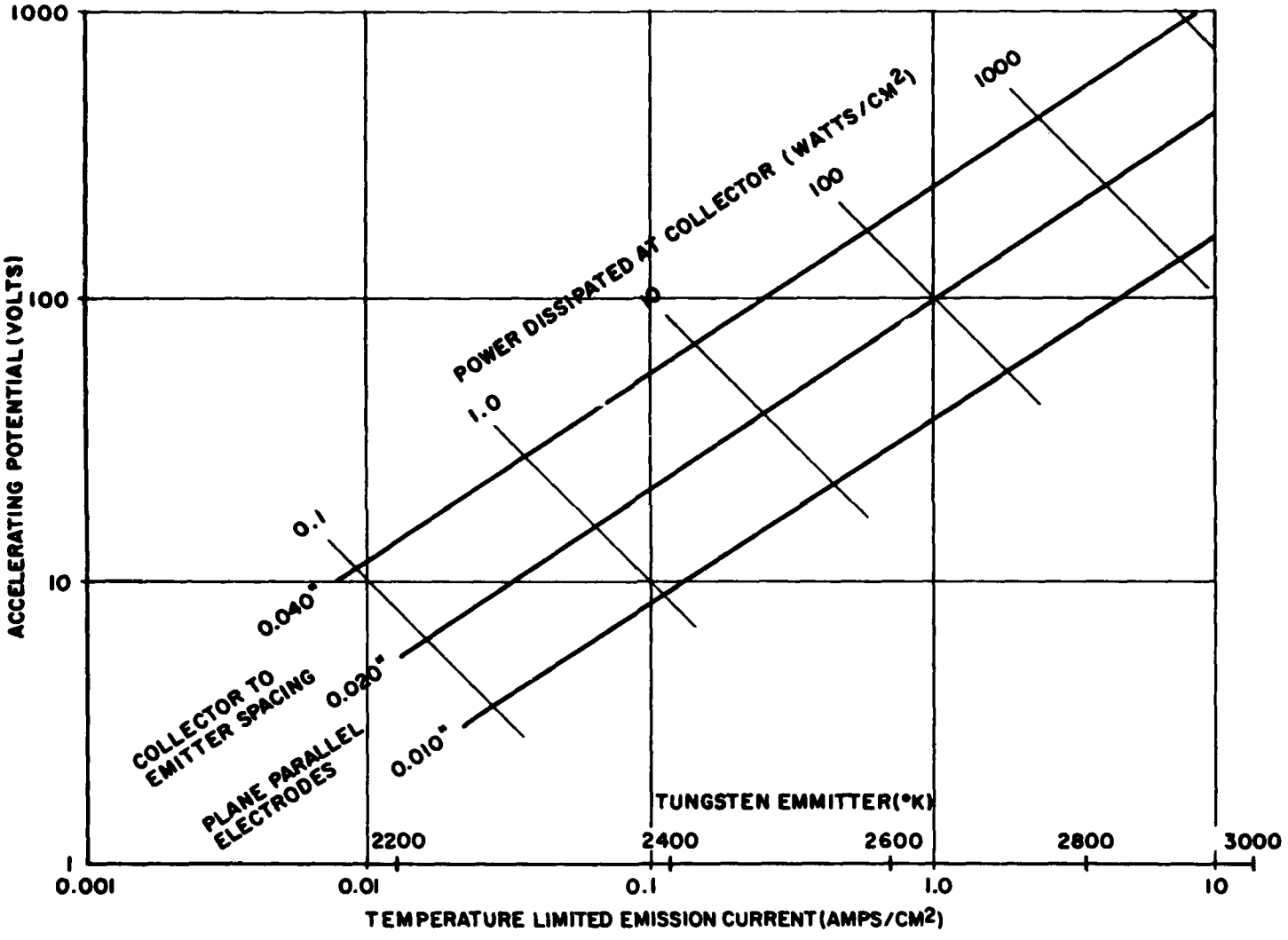

Figure 1. Thermionic Diode Power Dissipation

Taking the natural logarithm of both sides of the above expression and differentiating with respect to V_o, the following relation is obtained:

$$\frac{d \ln I}{d V_o} = \frac{-1}{kT}$$

It may be noted that the above expression is entirely independent of all thermionic constants. If the natural logarithm of the current is plotted vs retarding voltage, the slope of the line depends only on the temperature of the emitter and the universal Boltzman constant k; thus it permits direct measurement of absolute temperature.

b. "Open" Circuit Diode. The necessity of plotting thermionic current vs retarding voltage to obtain a temperature indication may be eliminated by operating a thermionic diode into a high impedance load which approximates an "open" circuit condition. An expression has been derived for the voltage V_O appearing across the terminals of a diode operating into a high impedance load.

By setting the current in the formula in subsection a, above, equal to V_o/R where R is the resistance of the high impedance load and V_O is the voltage generated by the diode, the following expression can be obtained after some algebraic manipulation.

$$V_o = kT \ln AT^2R - kT \ln V_o - \phi_2$$

where

k = Boltzman's constant 0.8616×10^{-4} eV/°K
T = emitter temperature in °K
A = constant = (theoretically) 120 amps/(°K)^2 cm^2
R = load resistance in ohms
ϕ_2 = collector work function.

Figure 2 shows V_O plotted as a function of temperature for load resistances of 5,000 and 10,000 ohms. It may be seen that the output voltage is quite linear with temperatures above 2000°K. It is relatively insensitive to changes in load resistance, and hence should be unaffected by moderate changes in the leakage resistance. Although independent of emitter work function, it is directly dependent on collector work function.

It appears that the major source of error in this type of temperature transducer will be due to changes in collector work function with time. If the collector runs comparatively cool, changes in the crystal structure with time and temperature should not be serious. Material that evaporates from the emitter and condenses on the collector will affect the collector work function, but if the emitter and collector are made of the same metal, the changes in collector work function with time should be minor, and the temperature indication should not be seriously affected.

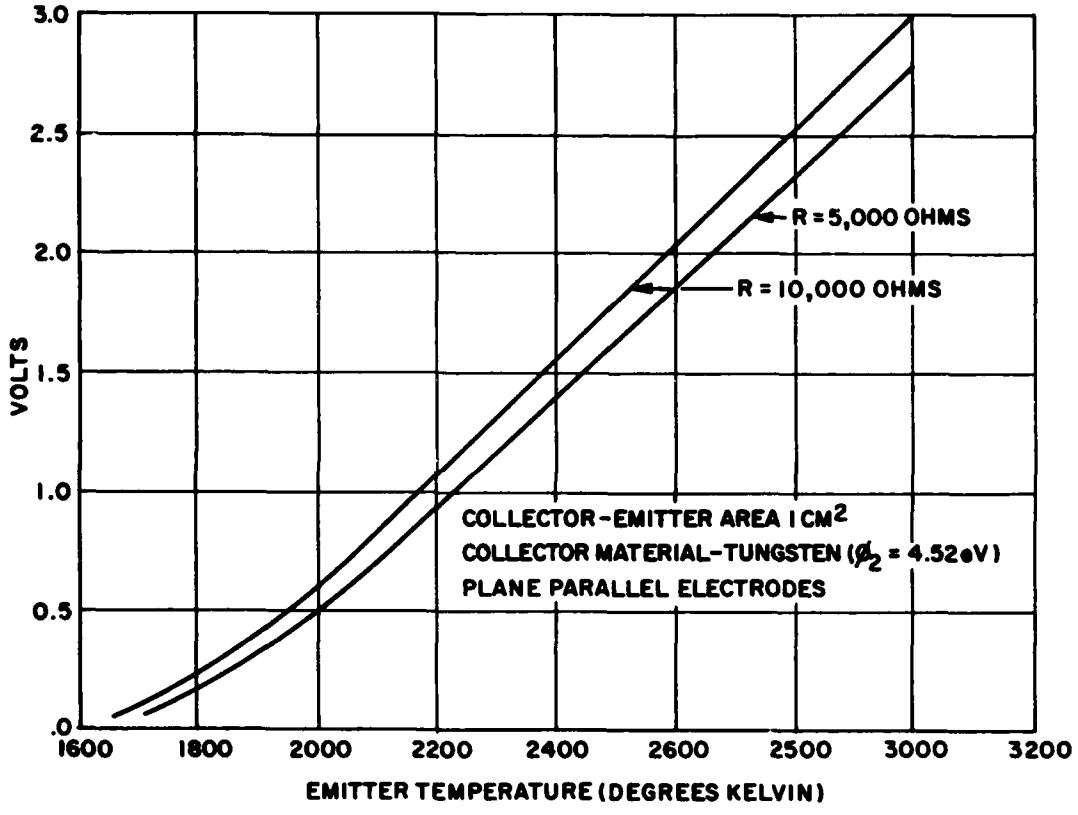

Figure 2. Open Circuit Diode Response

However, in the derivation of the expressions for operation in the retarding field region, it was tacitly assumed that the back emission from the collector was zero. In practice, this is usually achieved by operating the collector cold enough to reduce its emission to a negligible value. If this is done in a temperature transducer, the emitter will radiate heat to the collector at a rate close to that which would obtain with the collector at absolute zero because of the T^4 relation in the Stefan-Boltzman law. This will reduce the emitter temperature, causing errors in the indicated readout. Thus these techniques are not directly applicable to a thermionic temperature transducer.

The suppressor grid commonly used in a vacuum tube cannot be used here to reduce the back emission to zero. In the common vacuum tube, the electrons arriving at the plate have sufficient energy to pass through the retarding field set up by the suppressor grid. This energy is obtained because the plate (collector) is at a high positive voltage with respect to the cathode (emitter). In an "open" circuit diode, the collector is at a slight negative voltage with respect to the emitter. If a suppressor grid were to be used to eliminate back emission from the collector, the desired current from the emitter to the collector would be negligible because the electrons leaving the emitter with no more energy than that imparted by thermal agitation could not penetrate the retarding field set up by the suppressor grid.

c. Cancellation of Back Emission Current. A thermionic diode operating in the retarding field region may be used as a temperature sensor if means are found to either reduce the back emission to a negligible value or to cancel out the back emission current. Back emission will be negligible if the collector operates at a low temperature or if a high-work-function material is used for the collector. Operation of the collector at a low temperature will cause an excessive transfer of heat from the emitter to the collector, resulting in a lowered emitter temperature, as discussed previously.

Operation of a high-work-function collector, which necessarily must be of a different material than the emitter, at or near emitter temperature will result in both a negligible transfer of heat and a negligible back emission. However, this technique is not applicable to high-temperature operation since both collector and emitter material will evaporate and be deposited on the opposing electrode, and both the collector and the emitter will exhibit a composite surface with an uncertain work function that will vary with temperature and time. Hence, it is not feasible to reduce back emission by either of the above means.

However, a means may be available to cancel the effect of back emission. If a thermionic diode is operated in the retarding field region, the measured thermionic current will be

$$I = AT^2 \epsilon^{\frac{-\phi_2 - V_o}{kT}} - I'$$

where I' is the back emission current and the other factors are as defined in subsection a. The back emission current I' will remain relatively constant with changes in V_o if I' is the temperature-limited emission from the collector.

A means of instrumenting this technique is described in detail in Section IV.

3. DIODE OPERATION IN AN ACCELERATING FIELD

The thermionic current in the presence of a strong electric field is given by Spangenberg (Reference 1) as

$$I = I_o \epsilon^{\frac{-4.403E^{1/2}}{T}}$$

where

I_o = thermionic current at zero field
E = applied electric field in volts/cm
T = emitter temperature in °K.

The above relation is a mathematical expression for the phenomena known as the Schottky effect.

If I is measured for two values of E, I_o may be eliminated, and the following ratio obtained:

$$\frac{I_1}{I_2} = \epsilon^{\frac{4.403}{T}(E_1^{1/2} - E_2^{1/2})} \approx 1 + \frac{4.403}{T}(E_1^{1/2} - E_2^{1/2})$$

Since all coefficients in this equation except T may be measured with conventional electronic instruments, a means is available to measure temperature independent of all thermionic constants. This is in addition to the previously described technique of operating in the retarding-field region.

Several factors may militate against the use of this technique for temperature measurement, however. It cannot be used at elevated temperatures where the temperature-limited emission current is high because the combination of high current and high voltage will result in excessive power dissipation at the collector.

Any leakage currents in the transducer must be many orders of magnitude below the thermionic current to assure the desired accuracy in the indicated temperature. This technique cannot be used with a diode which has insulating members at a high temperature because the resistivity of insulators decreases rapidly with temperature. A material such as the oxides of aluminum, beryllium, or magnesium, which are excellent insulators at room temperature, becomes a semiconductor at the temperature of a tungsten emitter. For example, at 2000° K, the current density through the best of the insulators if of the same order of magnitude as the thermionic current density.

High energy electrons (10 volts and above) striking a cold collector cause it to emit secondary electrons which form a space-charge sheath in the neighborhood of the collector. If the collector operates close to emitter temperature, as it must in a temperature transducer so that it will minimize heat flow across the inter-electrode space, the collector will emit electrons thermally. This will produce a space charge even in the absence of high energy electrons, and will thus upset the current-voltage relationship known as the Schottky effect, since the field at the emitter will be a function of the space charge as well as of the applied voltage.

The magnitude of the Schottky effect is small. If 10 volts is applied across an interelectrode space of 0.1 centimeters to produce a field at the emitter of 100 volts per centimeter, the thermionic current will increase by only 2% for a tungsten emitter at 2000°K. Because of Schottky effect causes only a small perturbation in the thermionic current, it will be difficult to achieve high accuracy with this technique.

4. NOISE POWER DEVELOPED IN A DIODE

a. Theoretical Considerations. The noise current generated in a thermionic diode may be used to indicate the temperature of the emitter. The relationship between thermionic current and noise was originally derived by Schottky, and has been substantiated experimentally many times since. The following formula is from Spangenberg (Reference 1), but a similar derivation may be found in almost any standard text on vacuum tubes. The noise current i_n in a diode is:

$$i_n = \left[2 e I B (F_e)^2 \right]^{1/2}$$

where

e = electronic charge, 1.6×10^{-19} coulombs
I = thermionic diode current in amps
B = bandwidth of the noise spectrum in cps
$(F_e)^2$ = noise reduction factor.

The value of $(F_e)^2$ for temperature-limited emission is unity. For space-charge-limited emission, a representative value may be taken as 0.1 (Reference 3).

Figure 3 shows the noise current plotted as a function of thermionic current and bandwidth of the associated amplifiers for a temperature-limited diode, otherwise known as a saturated diode. This shows that the noise current is very small in comparison with the thermionic current, as should be expected since the noise is due to the variation in the arrival rate of electrons at the collector.

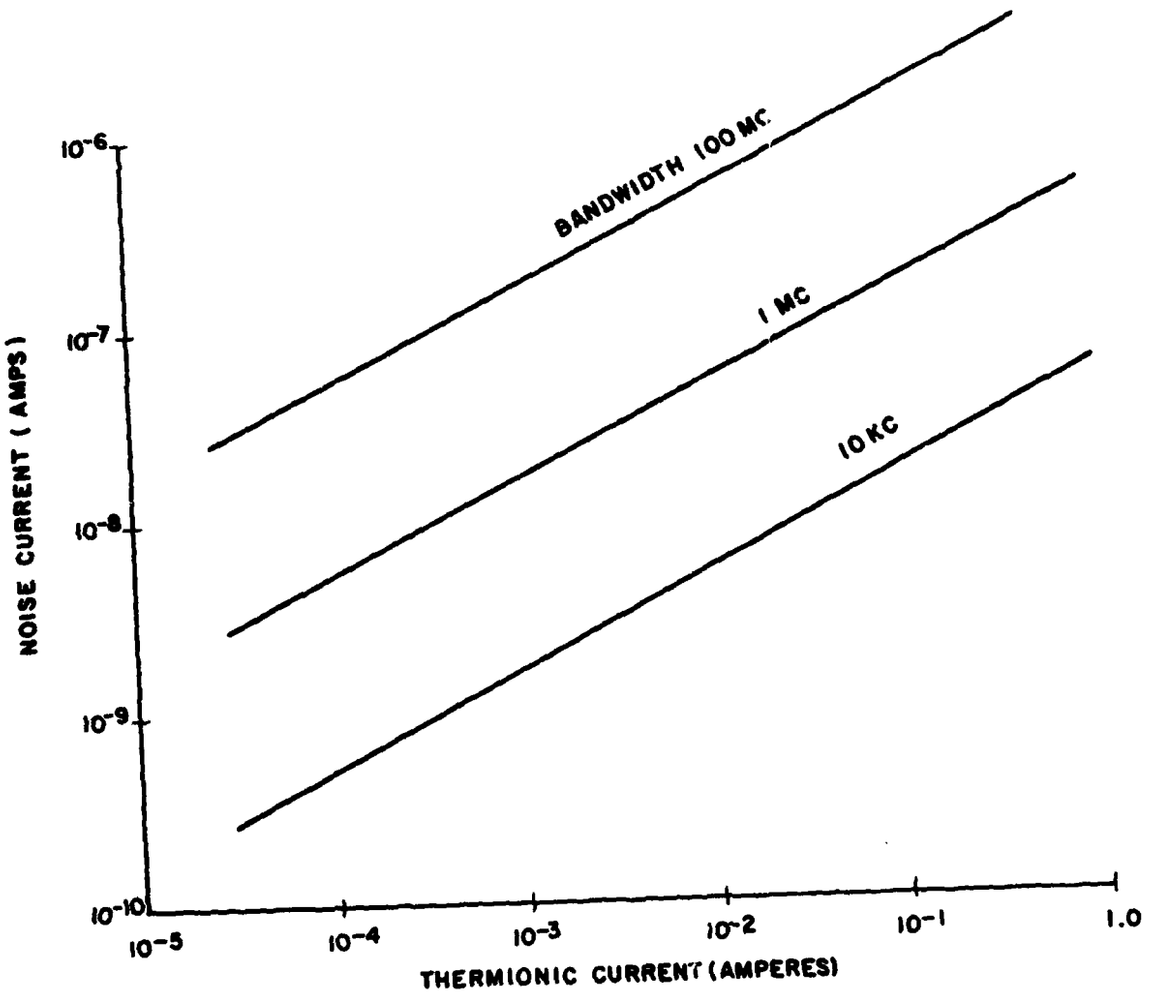

Figure 3. Thermionic Diode Noise Current

b. Experimental Results. Garrison and Lawson (Reference 4) achieved a reported accuracy of 1° by measuring the noise power generated in a resistor kept at 1000°C. The schematic of their system is shown and explained in Figure 4. To achieve the reported accuracy, it was necessary to use a filter in the detector circuit with a time constant of 2 minutes. Noise in the amplifiers was made to cancel by alternately switching between the hot resistor and an adjustable resistor kept at room temperature. The techniques used were suitable only for a laboratory measurement of noise power.

c. Speed of Response. In view of the long time constant used by Garrison and Lawson in their measurements, a theoretical investigation was conducted into the relationship between detector time constant and accuracy. Garrison and Lawson attribute the following relation for the rms error σ to Rice (probably S.O. Rice of the Bell Telephone Laboratories).

$$\sigma = (t\,B)^{-1/2}$$

where

t = time constant of detector in sec
B = bandwidth in cps.

On the other hand, Van Der Ziel (Reference 3) finds:

$$\sigma = (2\,t\,B)^{-1/2}$$

The latter value for the rms error is believed to be more representative of the error to be expected in an actual instrument in which integration of the rectified noise voltage is accomplished with an rc circuit whose time constant is t. The former value for the rms error is obtained when the rectified noise voltage is integrated over a period of time equal to t. For a more detailed discussion of the error obtained when measuring a noise voltage, the reader is referred to section 13.1 of the first edition of Noise by Van Der Ziel (Reference 3).

The rms error is plotted as a function of bandwidth and time constant in Figure 5. This shows that high accuracy and rapid response cannot be achieved simultaneously in a temperature indicator based on noise power. It should be realized that the accuracies shown in Figure 5 are absolute maximums that can theoretically be achieved. Actual performance should be expected to fall well below this figure.

d. Noise Power in Space-Charge-Limited Region. In the space-charge-limited region, noise power may also be used to measure temperature. In this region, noise power has the advantage of being independent of emitter work function because the current is limited by space charge. Since saturation current is not being drawn from the diode, the current and voltage requirements of the temperature sensor would be moderate. Thus is this region, noise power might have advantages.

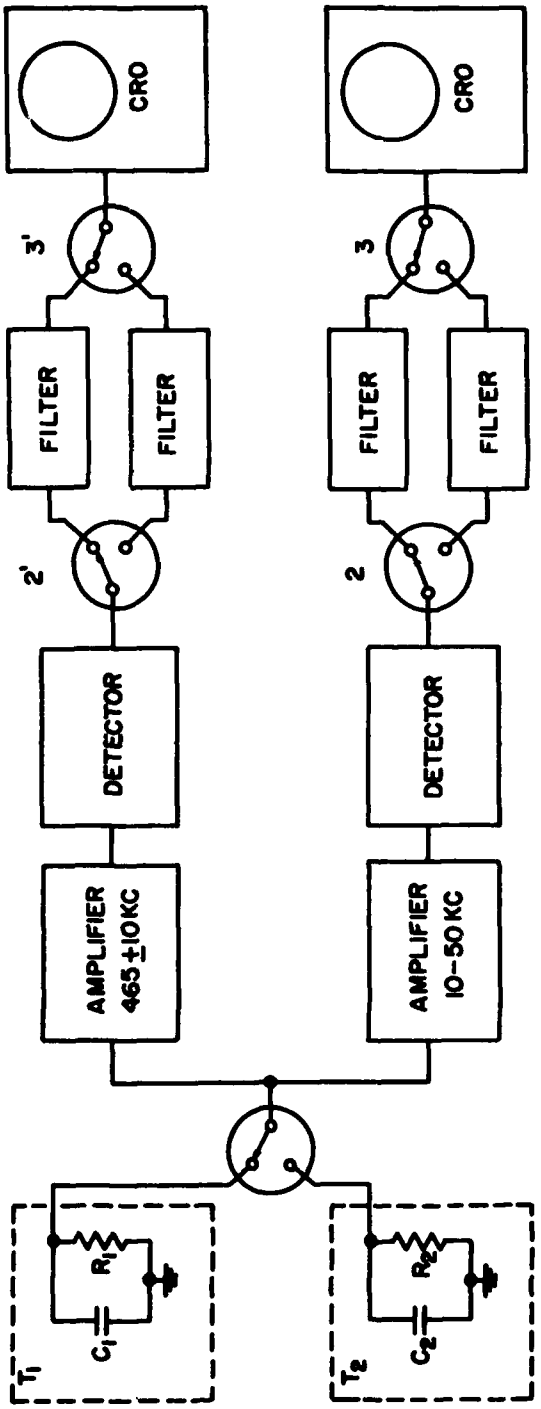

Figure 4. Noise Temperature Instrumentation

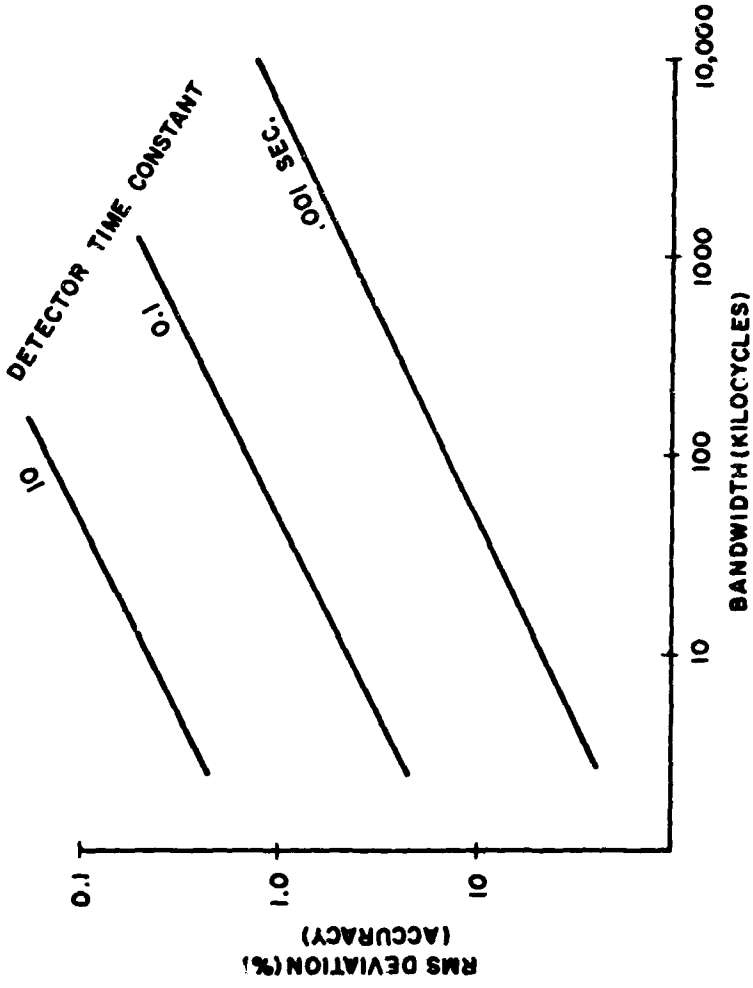

Figure 5. Accuracy of Noise Temperature Measurement

The magnitude of the noise power obtainable from a space-charge-limited diode is approximately that of a resistor at the emitter temperature with a resistance equal to the ac resistance of the diode (Reference 1). Even at high temperatures, approaching 3000° K, the available power is only an order of magnitude greater than that obtainable from a resistor of the same value at room temperature. The temperature dependence of the noise will be difficult to measure because of the noise introduced by the measuring equipment. In an experiment conducted in the laboratory, no temperature dependence whatsoever could be detected until the temperature-limited region was reached, indicating that sophisticated detection techniques are necessary.

5. DIODE OPERATION IN A CESIUM-VAPOR ATMOSPHERE

Company-funded attempts have been made in the past to build temperature sensors based on the operation of a diode in a cesium-vapor atmosphere. I was found that the sensors were extremely sensitive to cesium pressure as well as to emitter temperature but that they would not hold a calibration. This was probably caused by contaminant gases that were absorbed in the emitter and had not been driven out by previous heat treatments. The effect of absorbed gases on the emitter work function is discussed further in Section IV, where it is shown that a cesium-filled device will produce the same current for each of three different values of emitter temperature. Since previous experiments with cesium-filled devices have been disappoint'ng, and since the devices do not give a unique indication of temperature, this technique is not being considered for use in a temperature transducer.

6. BASIC CONCEPT CONCLUSIONS

The concepts based on temperature-limited emission current and on operation in a retarding field appear to warrant further investigation. Temperature-limited emission has been selected because of its extreme sensitivity to temperature changes. Operation in a retarding field is being investigated further because it shows the possibility of producing a temperature indication independent of changes in the thermionic work function.

Diode operation in an accelerating field does not appear to warrant further investigation despite its apparent ability to produce a temperature indication independent of all thermionic constants. Experimental data obtained under strict laboratory conditions show deviations from the Schottky effect, especially with respect to its temperature dependence. (References 2 and 5.) The small magnitude of the effect combined with the perturbations introduced by space-charge and leakage currents indicates that this concept cannot be used to construct an accurate temperature transducer.

The noise power associated with a thermionic diode is due to the random arrival of the emitted electrons at the collector. It is the ac component of a dc current; hence, it is orders of magnitude smaller than the thermionic current. At low or moderate temperatures where the thermionic current is not excessive, measurement of noise power offers no advantages and many disadvantages over direct measurement of the temperature-limited thermionic current. The major

disadvantage inherent in the measurement of noise power as an indication of temperature is the extremely low level of the noise and the resulting long time required to obtain a reading.

In the high temperature region (above 2500°K), noise power as an indication of temperature might appear to offer some advantages if obtained from a space-charge-limited diode. The electrical power requirements are moderate and the temperature indication is independent of emitter work function. However, the noise power available is very low, making an accurate determination of temperature difficult if not possible. Also, the construction of a temperature sensor to operate at or above 2500°K is at the present time not feasible because of erosion and/or corrosion of the envelope in any atmosphere except a nearly perfect vacuum. Therefore, noise power will not be considered further as an indicator of temperature.

Operation of a diode in a cesium-vapor atmosphere is also being eliminated from further consideration because it does not produce a unique indication of temperature and because experience with the concept in the past has been disappointing.

SECTION IV

THERMIONIC TEMPERATURE TRANSDUCER OPERATION IN RETARDING FIELD

1. THEORETICAL DEVELOPMENT

It has been shown in Section III that it is theoretically possible to obtain the temperature of a thermionic emitter independent of all thermionic constants when operating in the retarding-field region. The method of instrumenting the technique described below is predicated on the assumption that the back emission is temperature-limited and is therefore constant and independent of the retarding voltage applied to the diode.

It was also shown that the thermionic current I from a diode operating in a retarding field is:

$$I = AT^2 \epsilon^{\frac{-(\phi_2 + V_0)}{kT}} - I'$$

where

A = universal thermionic constant
T = absolute emitter temperature in °K
ϕ_2 = collector work function
V_0 = externally applied retarding voltage
k = Boltzman's constant
I' = back emission current.

The assumption is made that the back emission I' (emission from collector to emitter) is temperature-limited since the applied field for this direction of current flow is accelerating and all electrons that escape the collector reach the emitter. Since I' is constant, its effect on the current measurement may be eliminated by taking the difference between two levels of current, namely $I_1 - I_0$ and $I_0 - I_2$, where

I_0 is the value of current associated with a retarding voltage V_0

I_1 is the value of current associated with a retarding voltage $V_0 - \delta$

I_2 is the value of current associated with a retarding voltage $V_0 + \delta$

Algebraic manipulation yields the ratio

$$\frac{I_1 - I_0}{I_0 - I_2} = \frac{\epsilon^{\delta/kT} - 1}{1 - \epsilon^{-\delta/kT}} = \epsilon^{\delta/kT}$$

Let $$T = T_0 + \Delta T$$

then $$I_1 - I_0 = (I_0 - I_2)\, \epsilon^{\frac{\delta}{kT_0}} \left(1 - \frac{\delta}{kT_0} \cdot \frac{\Delta T}{T_0} + \ldots\right)$$

The expression for the thermionic current under a retarding field has been shown by others to hold for several decades of current. Hence, values of δ/kT_0 of as much as 10 could theoretically be used. With this value, the ratio of maximum to minimum current would be about 4×10^8, and the readout current would change 10% for a 1% change in absolute temperature. It is preferred that a value of no more than 3 be used for δ/kT_0 during initial testing of a device of this type to minimize errors due to nonlinearities that usually creep into a device the first time it is built. Substituting a value of 3 for δ/kT_0, the output current becomes

$$I_1 - I_0 \approx 20\,(I_0 - I_2)\,\left(1 - 3\,\frac{\Delta T}{T_0}\right)$$

From the above expression it can be seen that if $I_0 - I_2$ is held constant by electronic means, the output current $(I_1 - I_0)$ will be a function only of T, since T_0 is chosen arbitrarily along with δ so as to make δ/kT_0 equal to 3. The dynamic range required of the equipment is only about 400 to 1 and the sensitivity is reasonable in that the output indication changes three times as fast as the absolute temperature.

2. INSTRUMENTATION OF TRANSDUCER

The vacuum thermionic diode shown in Figure 6 receives voltages V_0, $V_0 - \delta$, and $V_0 + \delta$ successively from feedback amplifier 1. The current through the thermionic diode appears as a voltage drop across resistor R and is amplified by differential amplifier 2. The IR drop associated with voltage V_0 and noted on the diagram as I_0R is stored in the storage devices, which could be of the capacitor type, in front of differential amplifiers 3 and 4. It will be necessary to use lead-lag networks in conjuntion with the storage devices in front of amplifier 3 to ensure stability of the feedback loop, or some alternative means might also be used to ensure stability. The drops I_1R and I_2R associated with voltages $V_0 - \delta$ and $V_0 + \delta$, respectively, are also stored at the complementary inputs of amplifiers 3 and 4.

Amplifier 3 develops an output proportional to $(I_0 - I_2)R$, which is fed to differential amplifier 5. The other input to this amplifier is a reference voltage V_R. It may be shown that

$$(I_0 - I_2)R = V_R + V_0/G$$

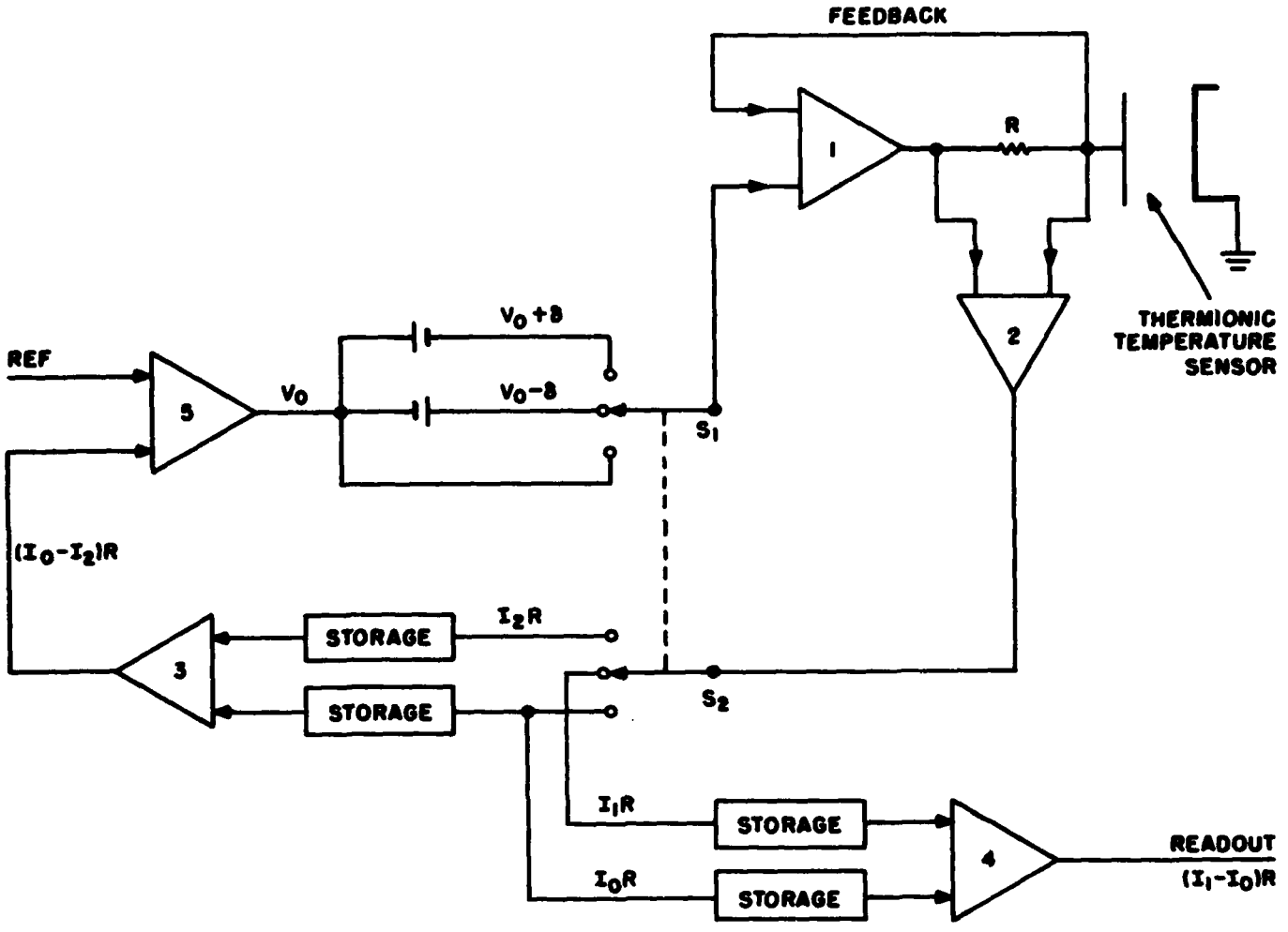

Figure 6. Thermionic Temperature Transducer Instrumentation in Retarding Field

where G is the gain of amplifier 5. For large values of G, $(I_0 - I_2)R$ approaches V_R, hence $(I_0 - I_2)R$ may be kept at a constant preset value except for an insignificant deviation.

Switches S_1 and S_2 operate simultaneously and ensure that the current associated with the proper voltage is stored on the correct storage device.

The output is $(I_1 - I_0)R$ and appears as a voltage at the output of differential amplifier 4. The current difference $I_1 - I_0$ is a function of the temperature of the emitter. It is independent of all thermionic constants as well as emitter area.

3. DISCUSSION OF SOURCES OF ERRORS

a. General. If temperature is measured by the application of a retarding field to a diode, the retarding field will be accelerating for back emission (from collector to emitter). If emitter and collector are constructed of the same material and are at approximately the same temperature, as they must be to form an accurate transducer, the back emission current will be much larger than the current from the emitter itself.

The instrumentation for temperature measurement in the retarding-field region assumes that the back emission current is independent of the value of the retarding voltage, $V_0 \pm \delta$, and that the back emission current may be eliminated by direct subtraction of two currents obtained at different values of retarding voltage. The validity of this assumption is questionable on the two counts; first, that at higher temperatures the value of $V_0 \pm \delta$ will be sufficient to overcome space charge effects, and second, that the temperature-limited current is independent of the accelerating voltage.

b. Effect of Space Charge. Calculations based on Child's law (Reference 1) for space charge between plane parallel electrodes show that for an interelectrode spacing of 0.050 cm, 1 volt is sufficient to overcome the space charge associated with a current density of $1 ma/cm^2$. Since $1 ma/cm^2$ is the saturation current density for a tungsten emitter at 2000°K, and the anticipated value of retarding voltage will be in the 1-volt range, it appears that saturation current will be drawn from the collector up to a collector temperature of 2000°K. Above this temperature, space-charge effects will be detrimental to operation in the retarding-field region. A higher retarding voltage will increase the temperature at which space-charge affects operation, but the increase will be insignificant because of the rapid increase of thermionic emission current with temperature.

c. Dependence of Back Emission Current on Voltage. Schottky has shown that the temperature-limited current is dependent on the accelerating voltage (Reference 1). At high field strengths, electrons with insufficient energy to overcome the work function barrier are "pulled out" of the surface of the emitter by the external field. For pure tungsten, the effect is small but measurable. For an assumed field strength of 20 volts per centimeter at the collector, the calculated increase in saturation current is 1% at 2000°K. Since the back emission is much larger than the emitter current being measured, any small percentage variation in the back emission will appear as a much larger percentage variation in the emitter current. This will lead to serious errors in the indicated temperature unless the effect can be calibrated out of the current measurements.

d. Electronic Circuitry. A numerical calculation for a hypothetical transducer using a tungsten emitter and collector at 1900°K showed that the back emission current was 20 times as large as the maximum emitter-to-collector current being measured and 8000 times as large as the minimum. Since the current being used as a temperature indication is only a small perturbation on a much larger current, a precision of one part in 100,000 would be required of the electronic circuitry to achieve an overall accuracy of 1/2 of 1% in temperature. Such accuracies would be difficult to attain.

e. Effect of Collector Temperature. Based on the assumption that the Schottky effect was valid for an accelerating voltage in the neighborhood of 1 volt, a calculation was made of the effect of collector temperature on the accuracy of the hypothetical transducer. This calculation showed that a change in collector temperature of 1 degree had the same effect on the indicated output as a change in emitter temperature of about 3 degrees. Thus, it may be seen that the device is more sensitive to collector temperature than to the emitter temperature that is to be measured.

It is most improbable that an accurate temperature transducer could be built based on the concept of operation in the retarding-field region. The basic reason for the lack of accuracy lies in the magnitude of the back emission current, which is many times the value of the currents that indicate emitter temperature. The obvious method of reducing the back emission by operating the collector at a low temperature cannot be used in a temperature transducer since this would lower the emitter temperature and result in an inaccurate temperature indication.

f. Conclusions Regarding Diode Operation in a Retarding Field. The instrumentation for the measurement of temperature by operating a thermionic diode in the retarding-field region eliminates back emission effects by the direct subtraction of two currents. The back emission current is not independent of retarding voltage, as has been shown by Schottky, and a subtraction of two currents cannot completely eliminate the effect of back emission. Due to the fact that the back emission current is much larger than the currents to be measured, small variations in back emission current due to the Schottky effect will lead to serious errors in the indicated temperature. This concept is being eliminated from further consideration.

SECTION V

FACTORS AFFECTING THE THERMIONIC WORK FUNCTION

1. EFFECT OF CRYSTAL STRUCTURE ON WORK FUNCTION

a. Work Function of Tungsten Crystals. Work function variations occur because of changes in the emitter surface on either a microscopic or a macroscopic scale. Such changes may be caused by crystal reorientation (grain growth) or by molecules of a foreign substance impinging on the surface and remaining there, either as a chemical compound or as adsorbed molecules. These effects may (and frequently do) cause large changes in the apparent work function of the emitter and/or collector

Work function variation with crystal orientation is exemplified by tungsten, upon which the greatest amount of experimental work has been done. Table I abstracts the work of two separate investigations (References 6 and 7) into the emission from various faces of a tungsten crystal.

Table I. Variations in Tungsten Work Functions

	Nichols			Smith		
Direction	ϕ	A_R	%	ϕ	A_R	%
111	4.39	35	+.38	4.38	52	+2.14
112	4.69	125	-1.37	4.65	120	-.67
116	4.39	53	+1.98	4.29	40	+.31
100	4.56	117	+1.20	4.52	105	+1.7
110	4.68	15	-9.20	4.58	8	-9.7

The above results indicate a variation in the work function ϕ of tungsten of approximately ±0.15 volts about a mean of 4.5 volts. However, the change in work function ϕ in general is partially offset by changes in the thermionic constant A_R, so that, except for direction 110, the variation in output current is less than would be expected from the variation in work function along. The % column shows the percentage error in indicated temperature at 2000°K compared with an assumed calibration based on $\phi = 4.50$ and $A_R = 60$. Note that except for the 110 face the indicated temperature is within ± 2% of a mean value for the different faces of a tungsten crystal.

b. Work Function of Polycrystalline Tungsten. An actual tungsten emitter exhibts a polycrystalline surface which, after sufficient aging, attains an equilibrium value with a work function of 4.52 volts. This equilibrium polycrystalline surface maintains itself despite temperature variations. For this reason, tungsten has been used extensively to experimentally determine the validity of the Richardson equation governing thermionic emission.

Additional experimental evidence that a properly aged tungsten emitter will maintain a constant work function over a long period of time is contained in tests run by Thermosen, Inc., on their temperature-limited diodes. N.H. Magida (Reference 8) quotes drifts of less than 0.5% over 1000 hours when the temperature-limited diode is used as a voltage regulator. If it is assumed that the only cause of drift is a change in work function, then it can be shown that the temperature of the emitter need change by only 1/4 of 1% over the 100-hour test period to compensate

for work function variations. A more probable cause of drift in the Thermosen tests is evaporation of the tungsten filament with time, and we may conclude that the work function variations were minor.

2. EFFECT OF ADSORBED GASES ON WORK FUNCTION

a. Theory. An emitter operating in a gas atmosphere of low vapor pressure will be subject to an arrival rate dN_1/dt of gas atoms, which is directly proportional to the partial pressure of the gas and is also a function of gas temperature and atomic weight. The rate dN_A/dt at which the adsorbed atoms build up will be equal to the difference between the arrival rate and the departure rate, dN_2/dt. In equation form this becomes:

$$\frac{dN_A}{dt} = \frac{dN_1}{dt} - \frac{dN_2}{dt}$$

The departure rate will be proportional to the number of adsorbed atoms, so let $dN_2/dt = KN_A$. After making this substitution and integrating, the following equation is obtained for N_A as a function of time t,

$$N_A = \frac{dN_1}{dt} \frac{1}{K} (1 - \epsilon^{-Kt})$$

It is an experimentally determined phenomenon that the value of K increases with temperature. This is illustrated by the fact that components of a high vacuum system are heated to drive off adsorbed gases. Thus N_A, the number of adsorbed atoms per square centimeter, will be a decreasing function of temperature. Since the adsorbed atoms affect the work function, N_A will certainly vary with emitter temperature if there are gases present capable of being adsorbed.

A work function which varies with temperature will still permit use of the thermionic emission current as a measure of temperature if the emission current is both repeatable and single valued. The speed of response, i.e., the length of time required to obtain an equilibrium value of adsorbed atoms, is also important.

b. Electronegative Gases. Experimental results on the effect of electronegative gases such as oxygen on tungsten are lacking due to the difficulty of controlling adsorbed gas layers. However, it has been observed that emission from tungsten which has been flashed at 2800° K to remove adsorbed gases decreases slowly at 1500° K in a vapor pressure of 10^{-10} mm of mercury with a time constant of the order of one hour. This is far too long to wait for equilibrium to be established in a temperature transducer.

c. Cesium Vapor. Considerable work has been done with electropositive cesium on tungsten by Langmuir and co-workers. A chart prepared by Langmuir is reproduced in Figure 7. This chart indicates that at a cesium pool temperature of 608°K, the arrival rate μ_o of cesium atoms at the emitter surface is 10^{21} atoms/cm^2/sec. Since a monolayer of cesium consists of approximately 5×10^{14} atoms/cm^2, a monolayer would be obtained in only 5×10^{-7} seconds. Thus the speed of response would be orders of magnitude greater than required. However, at 1200°K a current density of 16 amps/cm^2 is obtained, which would require several hundred volts at a collector-to-emitter spacing of only 0.020 inches to overcome space charge if there were no ionization. Actually, ionization occurs at only a few volts and the resulting current is magnified because of it.

At a lower cesium pool temperature, such as 412°K, the emission current will be only about 10 milliamperes at 1200°K, which requires only moderate voltages (less than 10 volts) to overcome space charge, and the speed of response will be adequate (less than a millisecond). It may be noted that due to the S shape of the curve, a current of 10 milliamperes is obtained not only at 1200°K but also at approximately 850°K and 2200°K. Temperature indication is therefore multi-valued, which renders a cesium-filled device useless at this cesium pressure for temperatures above approximately 900°K.

d. Other Electropositive Gases. The possibility exists that a thermionic diode can be operated in a vapor of some electropositive substance other than cesium. No experimental data in the form of S curves are available for such materials, so no conclusions can be drawn at this time. However, a few requirements for the theoretical vapor may be given. They are as follows:

(1) The arrival rate of molecules at the emitter surface should be of the order of 10^{17} molecules/sec to ensure that the time constant associated with obtaining an equilibrium surface does not exceed a few milliseconds. The vapor pressure corresponding to this arrival rate will be of the order of 10^{-3} mm of mercury.

(2) A vapor pressure of 10^{-3} mm of mercury should be attained at a temperature less than 800°K, which is safely within the capabilities of conventional metal-ceramic seals.

(3) The work function of the vapor should be approximately 4.0 volts to limit the emission current at 2000°K, and at the same time obtain adequate current at lower temperatures. A lower work function would be advantageous at low temperatures if at high temperatures with partial coverage of the emitter surface, the current-versus-temperature curve did not reverse slope, as it does with cesium on tungsten.

A possible candidate material for the vapor is magnesium. Its partial pressure at 650°K is 10^{-3} mm of mercury and its work function is 3.6 electron volts. Experimental thermionic data in the form of S curves such as those obtained by Langmuir for cesium on tungsten are lacking and probably never have been taken because magnesium, under ordinary circumstances, would never be considered for use as a thermionic emitter material.

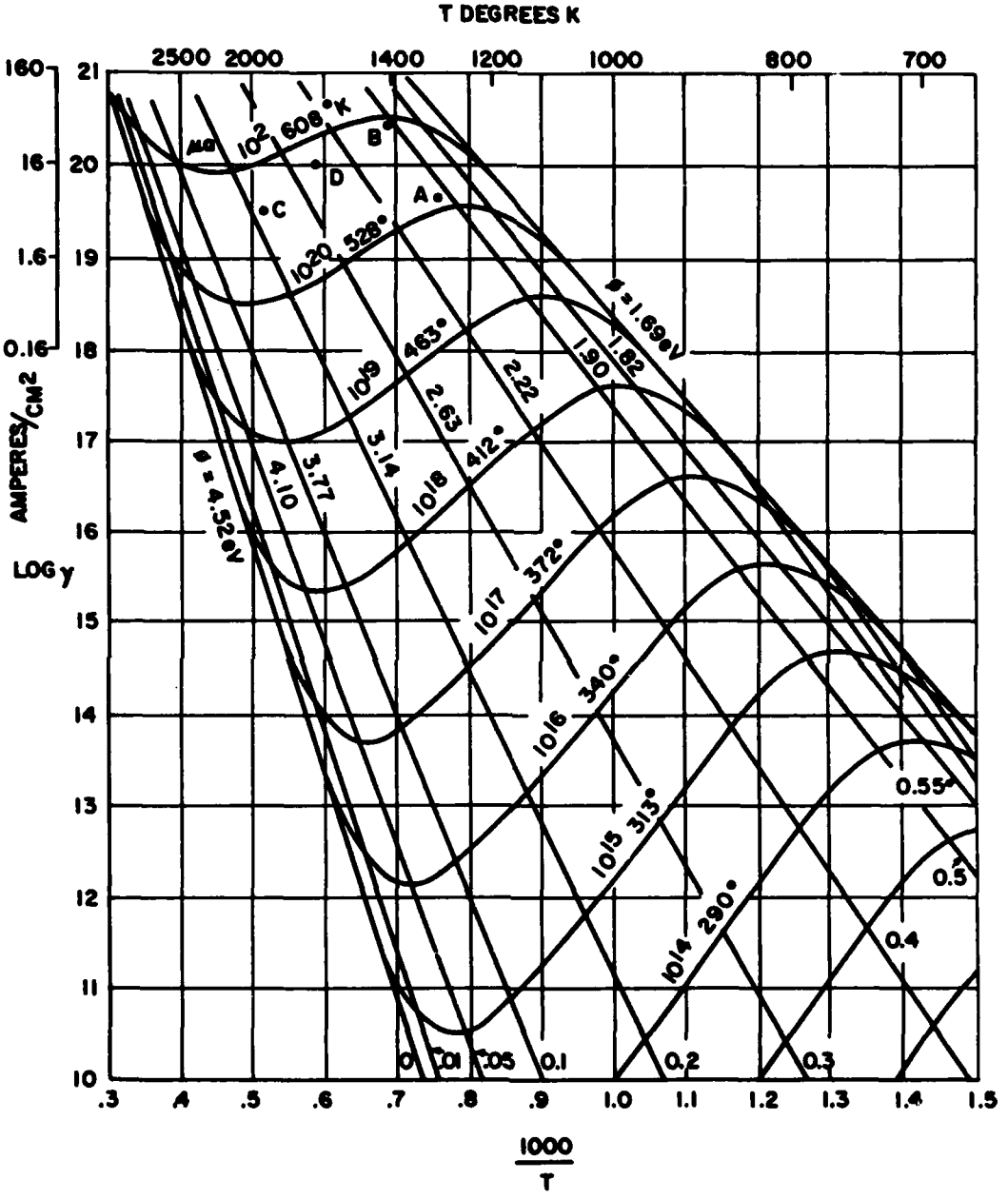

Figure 7. Cesium on Tungsten

Another possible candidate is barium. At 800°K its vapor pressure is 10^{-3} mm of mercury and its work function is 3.5 electron volts. It has been used in impregnated porous tungsten cathodes to reduce the work function of tungsten, but evaporates rapidly at temperatures above 1500°K, which is the desired lower limit for the temperature transducers. No S curves have been found for this material either and no conclusions can be drawn as to its suitability.

3. FINDINGS

It has been shown theoretically, and can be demonstrated by experimental evidence, that adsorbed atoms or molecules on the surface of an emitter will affect its work function. For tungsten, the experimental evidence shows a decreased emission when the emitter is poisoned by adsorbed oxygen and a greatly enhanced emission when it is covered (even partially) with cesium. Available test results on tungsten show very little variation in work function with time for an emitter used in a voltage regulator. (See Section V.1.b.)

The seeming inconsistency in the findings enumerated above is due to the fact that the enhanced and decreased emission phenomena occur at relatively low emitter temperatures (below 1500°K) while the emitter with the constant work function operates at a temperature in the 2000°K range. There are two possible reasons why the work function remains constant. First, the gas pressure in the voltage regulator tube was very low and was kept low through the use of appropriate getters. At low gas pressures, the arrival rate of gas molecules at the tungsten surface is low and the molecules are driven off by thermal agitation about as fast as they arrive; therefore not enough gas molecules remain on the surface at any time to appreciably affect the emission, provided the temperature is high. A second explanation (see Nottingham, Reference 2) points out that frequently a tungsten surface partially covered with adsorbed gas molecules is stable with time because the environment is well defined. He ends his discussion with the statement, "It must be emphasized that reproducibility is not a reliable indication of the absence of surface contamination."

Operation of an emitter in an atmosphere of barium or magnesium vapor might result in a clean, continuously renewed surface which would have a constant or at least a repeatable work function. This assumption is based on the supposition that the barium or magnesium vapor would remove any adsorbed molecules as fast as they appeared on the surface — a somewhat unlikely occurrence. Because experimental data on the thermionic properties of tungsten in an atmosphere of barium or magnesium are lacking, this approach should become the subject of a separate investigation.

SECTION VI

MATERIALS INVESTIGATION

1. CORROSION RESISTANT MATERIALS

a. General. It is anticipated that the thermionic temperature transducer will be used to measure skin temperatures on re-entry vehicles or exhaust temperatures in a rocket or a turbine. Accordingly, the materials investigation has considered only materials capable of existing for extended periods (approximately 100 hours) in an oxidizing and/or reducing atmosphere. The temperatures of interest are in the 1400°K (2000°F) range and above. Materials useful only at temperatures below 1400°K have not been considered.

The material or materials used in the hot zone of a thermionic temperature transducer must meet some very stringent requirements. In common with any other high-temperature structural material, it must possess adequate strength and resist corrosion and erosion at the temperature and in the atmosphere in which it will be used. In addition, it must resist permeation by atmospheric gases, since no contaminants can be permitted within the device.

Since the transducer must respond quickly to temperature changes, it must have a low thermal mass. If corrosion protection is gained through the use of resistant coatings, the coatings must also have a low thermal mass and high thermal conductance. Ablative coatings cannot be used since such coatings will not permit the underlying structure to attain the temperature of the gas environment.

b. Thermionic Converter Shell Development. A detailed investigation into high-temperature materials was performed by RCA for the United States Army Electronics Command, Fort Monmouth, N.J. (Reference 9). The work culminated in the development of a successful shell material for a thermionic converter operating in a fossil-fuel-fired atmosphere. Since their requirements and those of the temperature transducer are quite similar, the results of the investigation are reported in detail.

An extensive literature survey uncovered thirteen possible ceramics for coating refractory metals. Three ceramics, namely, alumina, beryllia, and silicon carbide appeared worthy of further investigation and were tested experimentally.

The results with silicon carbide were particularly disappointing. Samples of pyrolytic silicon carbide were eventually obtained from Texas Instruments, Inc., and from San Fernando Laboratories, but great difficulty was experienced in obtaining them. Delays of several months beyond scheduled delivery dates were encountered. The report states in part: "The fabrication problems were . . . associated with nonuniformity of deposition over the surface of the samples, internal stresses in the parts, difficulty in obtaining reproducible carbon mandrel material and, with deposition on a metallic substrate, poor bonding of the two layers."

Upon testing it was found that the permeation rate of gases through silicon carbide was considerably higher than through the alumina and beryllia samples. The material also cracked due to thermal shock, although no rapid temperature changes occurred.

Silica directly coated on a molybdenum cup, both with and without an outer layer of alumina, was tried and discarded. Another approach, which had been favorably reported in the literature, involved the use of a molybdenum — molybdenum-disilicide — silicon-carbide laminated barrier. The suppliers of this material were unable to produce satisfactory continuous coatings.

Beryllia, which has a low permeation rate, spalled badly in a fossil-fuel gas environment. At the conclusion of the test, the burner parts and the exhaust hood were covered with a thin layer of beryllium oxide, which is toxic.

Alumina bonded directly to a metallic substrate cracked when heated because of a difference in the coefficients of expansion between the coating and the metal. When operated as a self-supported shell, alumina had a low permeation rate, did not show corrosion in a fossil-fuel gas environment, and withstood repeated thermal cycling.

As a result of their studies into emitter shell materials, RCA designed a thermionic converter using an outer shell of alumina separated from the molybdenum emitter by a layer of inert gas. This separation introduced a high thermal resistance between the alumina and the emitter, causing a temperature drop of 200°C across the gas. It should be noted that they were forced into the double-wall construction because of a complete lack of success with corrosion-resistant coatings bonded directly to the emitter. Such a shell, because of the large temperature drop across the inert gas layer, would be completely unsatisfactory as an accurate temperature transducer.

c. Refractory Metal Coatings - State of the Art. An excellent review of the state of the art of refractory metal coatings is available in a paper written by J.K. Elbaum and N.M. Geyer of the Air Force Materials Laboratory (Reference 10). They state ". . .tantalum coatings require more extensive evaluation, and tungsten coatings have only very recently become available."

The paper then explains that very little evaluation of any of the high-temperature coatings has been conducted in environments other than atmospheric air at 1-atmosphere pressure. Some limited testing on silicide and aluminide coatings at 1 mm of mercury has indicated a greatly reduced life at low pressures. Tests have also shown that slow excursions between low and high temperatures cause premature failure and that failure will occur sooner at an intermediate temperature.

A curve representative of lifetime versus temperature for a typical silicide coating is shown in Figure 8. This is the general shape of curve to be expected with the silicide coatings that have thus far shown themselves to be the most satisfactory. Note particularly that there is a region of minimum performance at a temperature below the normal operating temperature.

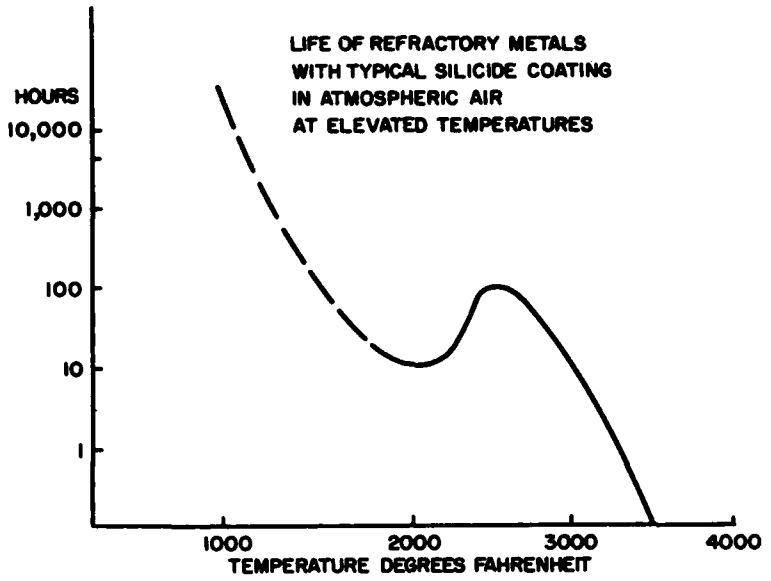

Figure 8. Silicide Coating Temperature Characteristics

A theoretical discussion of the mechanism by which protection is achieved will help explain the findings reported by Elbaum and Geyer. Let us specifically consider the silicide coatings on a refractory metal.

A refractory metal oxidizes easily at elevated temperatures, and a coating is required that will protect the metal surface from oxidation. Silicon either in the metallic form or as a compound provides such protection because at high temperatures it oxidizes to SiO_2, which forms a viscous, glassy coating that protects the underlying metal. At lower temperatures, the coating becomes brittle, small cracks form, and the underlying metal oxidizes. At low ambient pressure, the coating evaporates more readily, since there is no external gas to inhibit evaporation, and gases dissolved in the coating are released and form bubbles. If the bubbles break, direct contact occurs between atmospheric air and the underlying metal. Thus failure will also occur sooner at low ambient pressures as well as at the intermediate temperatures at which the SiO_2 is brittle.

d. Platinum Coatings. The platinum group of metals exhibits pronounced resistance to oxidation at elevated temperatures and might be plated onto a refractory metal to prevent oxidation of the substrate. This approach was tried some years ago but the lifetime of the coatings at 1400° K was found to be only a few hours (typically 10) rather than of the expected lifetime of thousands of hours. The failure mechanism consisted of diffusion of oxygen through the platinum coupled with diffusion of the substrate through the platinum coating.

At the present time, Texas Instruments, Inc., under Navy sponsorship (Reference 11), is conducting a program to develop barriers that will prevent interdiffusion of the platinum coating and the substrate metal. Although they are presently working with columbium and molybdenum, it is anticipated that the results will also be applicable to tungsten and tantalum. Their investigations will not be completed in time to be of use in our current development of a thermionic temperature transducer.

e. High-Temperature Tungsten Coatings. A high-temperature coating for tungsten has recently been reported (Reference 12) which indicates that a quantum jump may have taken place in the state of the art for protective coatings. The following description has been copied verbatim from the reference.

> Metal Bonded Oxide Coatings for Tungsten
>
> A family of coatings have been developed to prevent catastrophic oxidation of tungsten up to at least 3500° F. Laboratory experiments and limited process scale-up have demonstrated excellent potential for these coating systems, not only for protecting tungsten but other refractory metals as well.
>
> The coating is applied in one or more steps, depending upon the variation desired, by a halide-activated vacuum pack process. Diffusion alloying takes place during deposition, and the result is a relatively thin (2-mil) layer which imparts extremely high oxidation resistance by formation of a dense, adherent ceramic coat during oxidizing exposure. Co-deposition of two elements simultaneously is used to obtain the desired microstructure and chemistry. Laboratory programs have shown two compositions of particular interest to be (Si-W) and Ti-Zr-(Si-W).
>
> Mechanical tests conducted in vacuum at 3300° F on 60-mil coated sheet specimens, oxidized in air for one hour at 3300° F, possess the following properties:

Coating	U.T.S. (PSI)	0.5% QS (PSI)	R.A. (%)	Elongation (%)
(Si-W)	8,790	5,190	98	103
Ti-Zr-(Si-W)	8,280	5,250	98	49

Oxidation testing has shown the (Si-W) coating to be protective for 75 to 100 hours at 3000° F, for 12 to 16 hours at 3300° F, and two hours at 3500° F, in air under thermal cycling conditions. The Ti-Zr-(Si-W) system has protected tungsten 50 to 75 hours at 3000° F, 10 to 12 hours at 3400° F and 2 hours at 3600° F. Both systems have also been tested by exposure to simulated air arc plasma jets at temperatures up to 3500° F for elapsed times as long as 2 hours, with six twenty-minute thermal pulses, without failure. Oxidation tests at pressures simulating re-entry conditions have also been run on both coatings at 3400° - 3500° F for as long as an hour without failure.

Excellent promise is seen for applying these coating systems to refractory metals other than tungsten. Molybdenum has already been coated directly with the W-Si system, and development work is continuing on coating columbium and tantalum alloys. The technique used is to pre-coat the refractory alloy with tungsten and then proceed as if the substrate alloy were tungsten.

LIMITATIONS: Processing requirements presently limit the use of the coatings to parts which will fit within the 18 inch high x 7 inch diameter furnace retort at Thompson Ramo Wooldridge. Also, there is significant degradation of low temperature mechanical properties of tungsten due to recrystallization during the coating process, but this degradation is not evident at the higher potential service temperatures. There remains some possible speculation regarding protective reliability of these coatings in the absence of statistical test evaluation, particularly at temperatures below 2000° F.

This coating appears promising for use in air although its lifetime may be slightly under the desired 100 hours. A second factor that may militate against its use is the implication that its reliability may be uncertain at temperatures below 2000° F.

f. Findings. It is reasonably certain that no single coating will ever be found that will withstand all possible environmental atmospheres at elevated temperatures. The coating to be used in a particular environment will perforce have to be tailored to meet that environment. Bearing this in mind, coatings were considered on the basis of their performance in atmospheric air, since this is the only test environment in which substantial data of a favorable nature have been accumulated.

At this time, no coating can be recommended as having a lifetime of 100 hours at 2775°K, as required in the objectives. The closest approach to these requirements is the coating developed by Thompson Ramo Wooldridge that has a reported life of 75 to 100 hours at 3000° F (1925°K) in atmospheric air. While this temperature is well under the requirements, it is by far the best that has been reported to date. It is therefore recommended for use in the temperature transducer.

Because of the extensive research performed by RCA, and their pronounced lack of success in developing a coating for use in a fossil-fuel-gas environment, no recommendations are being made for a coating material for use in exhaust gas atmospheres at this time.

2. EMITTER AND COLLECTOR MATERIALS

a. General. The collector of a thermionic temperature transducer must operate at a temperature close to that of the emitter to minimize the transfer of heat across the interface. Heat flow from the emitter to the collector must be obtained from the source whose temperature is being measured.

Such a flow will cause the emitter to indicate a erroneous temperature that is below the true temperature of the source, the magnitude of the error being a function of the heat flow and the thermal resistance of the source. To minimize the error, it is necessary to minimize the heat flow by operating the collector as close to emitter temperature as practical, since the thermal resistance of the source is not subject to control by the designer of the temperature transducer.

Because both emitter and collector must operate at an elevated temperature, consideration must be given to the evaporation of material from both. Figure 9 shows the evaporation rate of selected thermionic materials expressed in time required to evaporate a monolayer. At 2000°K this varies from a few seconds for hafnium and iridium to 100 hours for tungsten, the most refractory metal known. Since the molecule arrival rate of one electrode will approximately equal the departure rate at the other electrode, it can be surmised that the probability exists of more or less rapidly altering the nature of the electrode surfaces if the materials are dissimilar. However, if the two electrodes are made of similar material, there will be but slight alteration of their work function with time since there will be no foreign molecules available to contaminate their surfaces. Therefore, both collector and emitter should be constructed of the same material.

b. Selection of Emitter Material. Figure 10 is a plot of all metals with a melting point above 2000°C except protactinium, boron, and technetium, for which no data are available and which are not obtainable in structural shapes. Work function ϕ is plotted against T_e, the temperature at which the vapor pressure is 10^{-5} mm of mercury. The metals of interest are those with the highest T_e at a given work function. A glance at the chart shows that hafnium, tantalum, and tungsten should be considered.

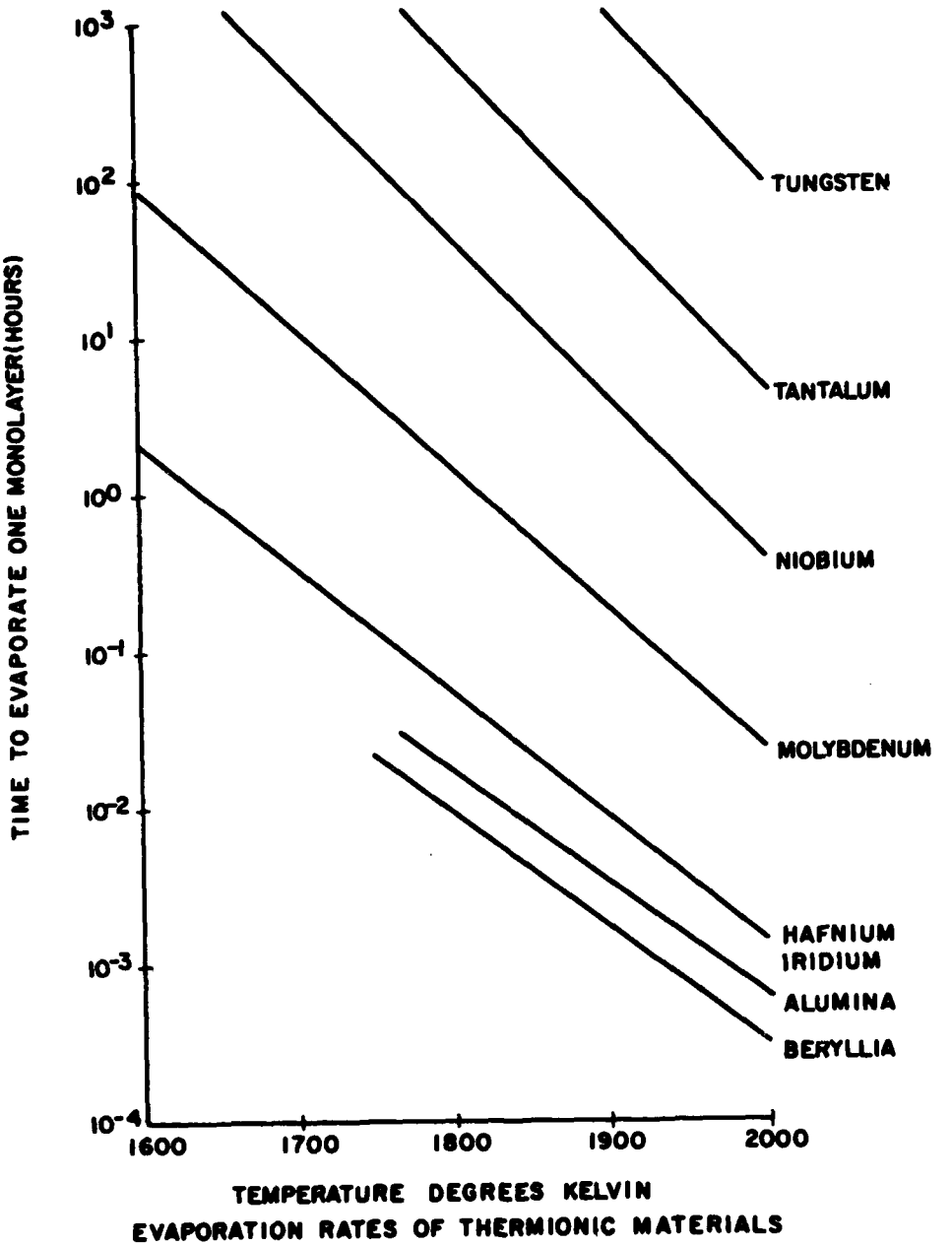

Figure 9. Evaporation Rates of Thermionic Materials

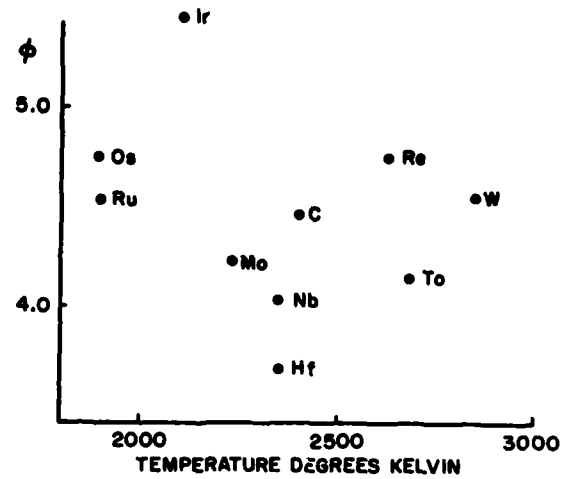

Figure 10. Work Function of High-Melting Point Metals

Hafnium is a metal with a comparatively low work function (3.65 volts) and should be excellent for use below 2000° K where the saturated emission current from tungsten is less than one milliampere per cm^2. Previous attemps to use hafnium as an emitter have shown that it is subject to poisoning by adsorbed gases which cannot be expelled by repeated operation at temperatures as high as 2150° K (Reference 13). Its work function is variable and increases with the irreversible sorption of gases, and it would thus be unsatisfactory for use as an emitter in a temperature transducer operating in the temperature-limited mode. It has therefore been eliminated from consideration for this program.

Tantalum might be satisfactory as an emitter in a thermionic temperature transducer. Its mechanical properties are similar to those of steel, so fabrication of complicated shapes should not be difficult. It is possible to outgas the metal by heating it to 2300° C, but complete elimination of all gases requires a higher temperature.

Tantalum readily absorbs gases above 600° C (Reference 14), and is actually used as a getter in vacuum tubes. It is much more difficult to outgas than tungsten, requiring a temperature of 3100° K to completely eliminate the absorbed oxygen. Probably it will readily absorb oxygen, which would alter its work function at any temperature up to 2500° K, which is beyond its useful range as an emitter due to the high voltage required to overcome space charge. For this reason it is being discarded in favor of tungsten.

Tungsten is an excellent emitter at high temperatures and may be easily outgassed by flashing at a temperature of 2600° to 2800°K. It is available in structural shapes although unconventional fabrication techniques will be necessary to obtain specific structural forms. At low temperatures, it exhibits a low value of saturated emission current due to its high work function (4.52 volts), and is subject to poisoning by residual gases present in the interelectrode space. On the basis of available information it appears to be the best material for use as an emitter in a thermionic temperature transducer because it can easily be outgassed, is available in structural shapes, and has a very low vapor pressure. It has therefore been selected for use in the temperature transducers to be designed under this program.

SECTION VII

TRANSDUCER DESIGN

Three transducers, two for gas and one for surface thermionic temperature measurement, were designed in an effort to arrive at a practical device. Some previously undiscussed problems that beset a thermionic temperature transducer are definition of the area of the emitter, and reduction of the heat flow by conduction along the transducer to a level that will not excessively reduce the emitter temperature. Design No. 1 is a relatively simple and rugged transducer in which the method of defining the emitter area is questionable, design No. 2 accurately defines the emitter area but is fragile, while design No. 3 is that of a surface transducer which excessively robs heat from the source.

1. DESIGN OF TRANSDUCER NO. 1

The mechanical design of this transducer, shown in Figure 11, is both simple and reasonably rugged for a thermionic device, and if a thermionic temperature transducer is to compete with conventional transducers such as thermocouples or resistance thermometers, its design should not be appreciably more complex than that shown. In this design the emitter area is defined by the simple expedient of using a high-temperature ceramic to insulate the portions from which emission should be suppressed. The ceramic is in the form of a sleeve that is not bonded to either the collector or the emitter. This eliminates any problems that might arise from differences in thermal expansion rates.

Selection of the ceramic is based on low vapor pressure and high resistivity at elevated temperatures. Two equally attractive candidate materials are beryllia and alumina. However, Kohl (Reference 14) indicates that on the basis of reactivity with emitter materials, beryllia should be used with tungsten and alumina with tantalum.

Tantalum, because of its lower work function (4.1 vs 4.52 volts), will exhibit a saturated emission an order of magnitude above that of tungsten. It appears that this would be advantageous because of the low resistivity of the ceremics at high temperatures, which is of the order of 10,000 ohm-cm (Reference 15). However, much of the advantage is lost because a higher voltage would be required to overcome space charge in accordance with the Child-Langmuir law. The higher voltage would increase the leakage current and the ratio of thermionic current to leakage would be only twice as great for tantalum as for tungsten.

Although Kohl states that tantalum may be used in contact with alumina up to 1900°C, he also mentions an experiment in which tantalum reduced alumina at only 1000°C when the two materials were in contact, and another experiment in which the reaction began at 1600°C when the materials were not in physical contact. He further states that this reaction does not occur with tungsten. Therefore, on the basis of chemical activity with a ceramic vapor, tungsten has been selected as the emitter material with a beryllia ceramic. Kohl gives 2000°C

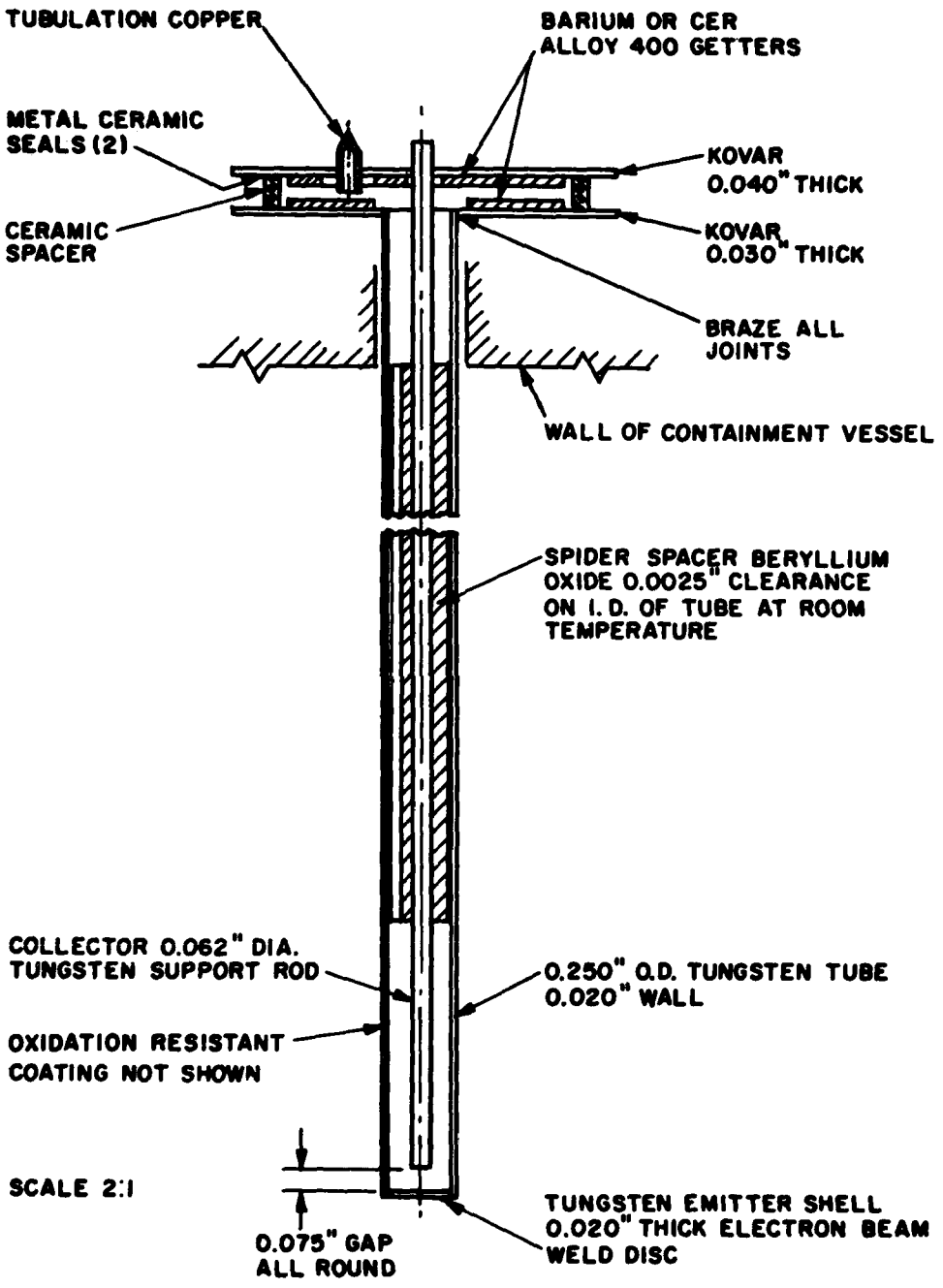

Figure 11. Gas Temperature Transducer No. 1

(2273° K) as the upper limit for this combination when used as the heating element in a vacuum furnace. This limit will be much lower, however, for a thermionic emitter since even a slight degree of contamination on the surface will affect the work function of the emitter.

Some difficulty is anticipated with this design because the relatively high vapor pressure of the ceramic will fill the interelectrode space with ceramic vapor. At the equilibrium ceramic vapor pressure corresponding to 2000° K, the emitter will be bombarded with ceramic vapor at a rate sufficient to build up a monolayer in approximately 1 second. It is anticipated that at this temperature, the equilibrium emitter surface will be covered with considerably less than a monolayer of ceramic; therefore, a stabilized surface will build up in considerably less than 1 second. If the ceramic vapor does not unduly poison the emitter, operation as a temperature sensor in the 2000° K range should be satisfactory.

At lower temperatures, the vapor pressure will be less while the percentage of coverage of an equilibrium surface will increase, and long time constants (on the order of an hour at 1600° K) will be required to attain an equilibrium surface. Obviously, such long time constants would render the device unsatisfactory as a temperature transducer at the lower temperatures.

A possible solution to this difficulty lies in the use of a getter material operating at a temperature that will produce sufficient vapor pressure to ensure complete coverage of the emitter. A candidate material is barium, which at 300° C is an excellent absorber of gases and develops a vapor pressure (10^{-5} mm of mercury) sufficiently high to ensure an equilibrium emitter surface in a fraction of a second.

However, our experience with cesium has shown that if the surface coverage is less than 100%, the effective work function of the partially covered surface is highly dependent on the degree to which the underlying surface has been poisoned. It is most unlikely that full surface coverage could be obtained on a hot emitter operating close to the boiling point of barium. Since no data on the actual surface coverage of barium on tungsten were found, this possible solution is being dropped at this point.

2. DESIGN OF TRANSDUCER NO. 2

The anticipated difficulties due to a high vapor pressure of the ceramic insulation in design No. 1 may be avoided by use of a guard ring that will accurately define the active area of the emitter. Such a design is shown in Figure 12. It may be noted that this transducer is considerably more complicated than that in Figure 11 because of the necessity of bringing out a separate lead from the guard ring and the requirement that there be no ceramic insulation in the hot zone of the transducer.

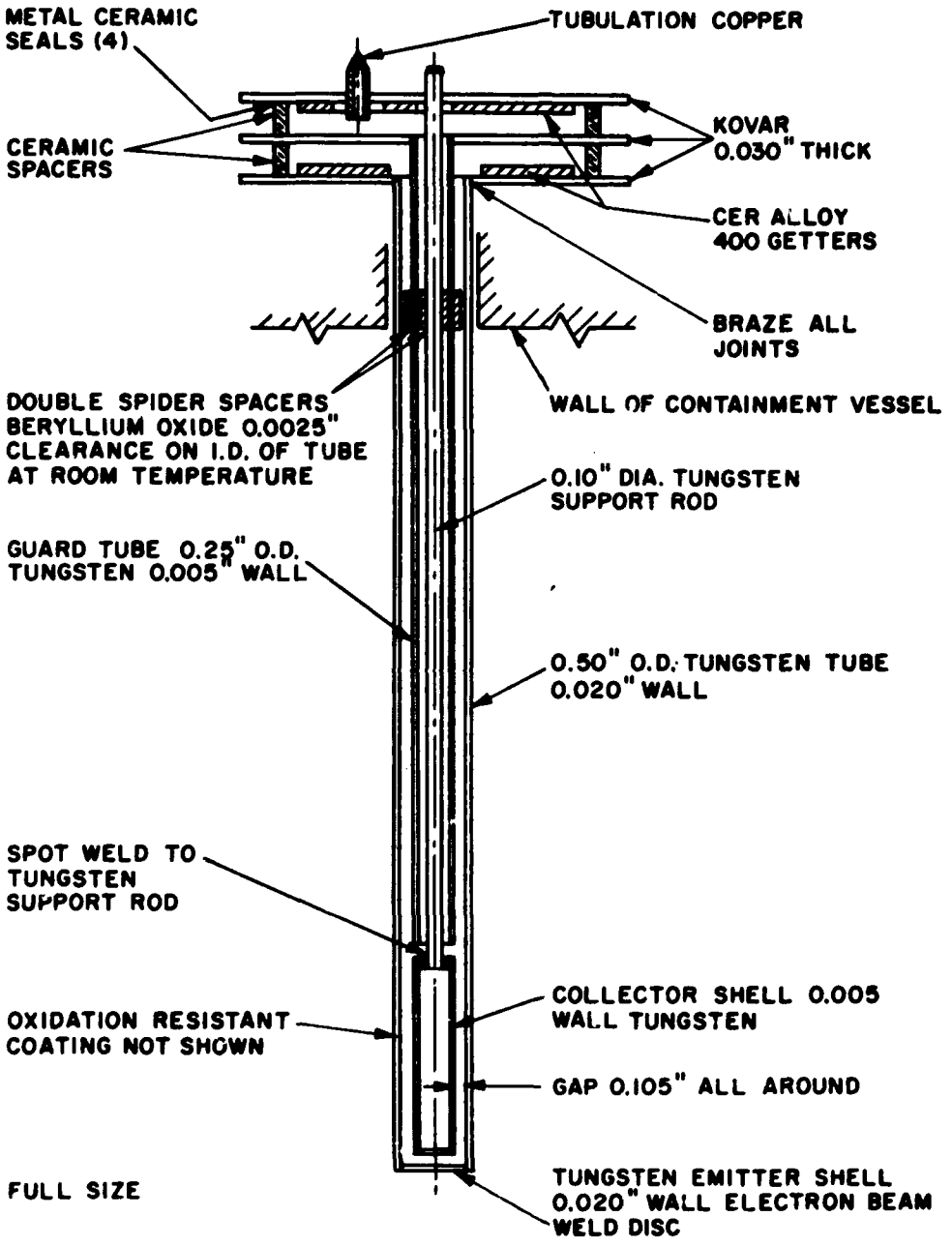

Figure 12. Gas Temperature Transducer No. 2

It was originally anticipated that it would be possible to operate a guard ring at emitter potential, but at a temperature at least 200°K below that of the emitter. The density of the emission current from the cooler guard ring would be considerably less than that from the emitter and would not seriously increase the total emission current. A sample calculation based on equal areas for a tungsten emitter at 2000°K and a guard ring at 1800°K showed that the total current from the guard ring and the emitter was equivalent to the current obtained from an emitter at 2004°K. Since much of the error could be calibrated out of the reading and since the actual guard ring area may be made less than that of the emitter, the actual temperature error in the output indication would be negligible.

A heat transfer study was made to determine emitter temperature distribution in the presence of a guard ring whose temperature was 10% less than peak emitter temperature measured in degrees Kelvin. Because of the complexity of the problem, an electrical analog of the temperature transducer was constructed to verify the answer to the thermal problem. Under optimum conditions of heat transfer, i.e., with gas flowing past the transducer at sonic velocity coupled with highly reflective surfaces inside the transducer to reduce radiation losses to the shield, the average temperature of the emitter was about 1% under the gas temperature. At lower values of heat conduction (gas to emitter), such as would be obtained at 25% of sonic velocity, the error will increase to more than 5%. This type of guard ring will therefore not be satisfactory for an accurate temperature transducer.

The transducer shown in Figure 12 incorporates a guard ring of very thin material, 0.005 inches being specified on the drawing. The thin material will provide a path with high thermal resistance back to the heat sink and thereby permit the guard ring temperature to approach emitter temperature, reduce the radiant heat losses to a minimum, and permit the emitter to more nearly approach the gas temperature. The guard ring will operate at collector potential to eliminate current interchange between it and the collector. The collector, obtaining current only from the hot portion of the emitter, may yield a current that is an accurate measure of emitter temperature.

A test run on an electrical analog of this transducer showed a significant increase in the average emitter temperature over the previous design. The average emitter temperature was less than 0.5% under the gas temperature and much of this error could be calibrated out of the reading for an operational transducer.

3. DESIGN OF SURFACE TRANSDUCER

A design for a surface-temperature transducer is shown in Figure 13. The emitter is designed to be placed against the material whose surface temperature is to be measured. Assuming excellent thermal contact between the emitter and the surface, the current output of the transducer will be a function of surface temperature. An unresolved problem with this transducer is the means of obtaining the thermal contact necessary for accurate temperature measurement. One method of obtaining excellent thermal contact is to use a material in the interface that will be liquid at operating temperature and will wet both the emitter

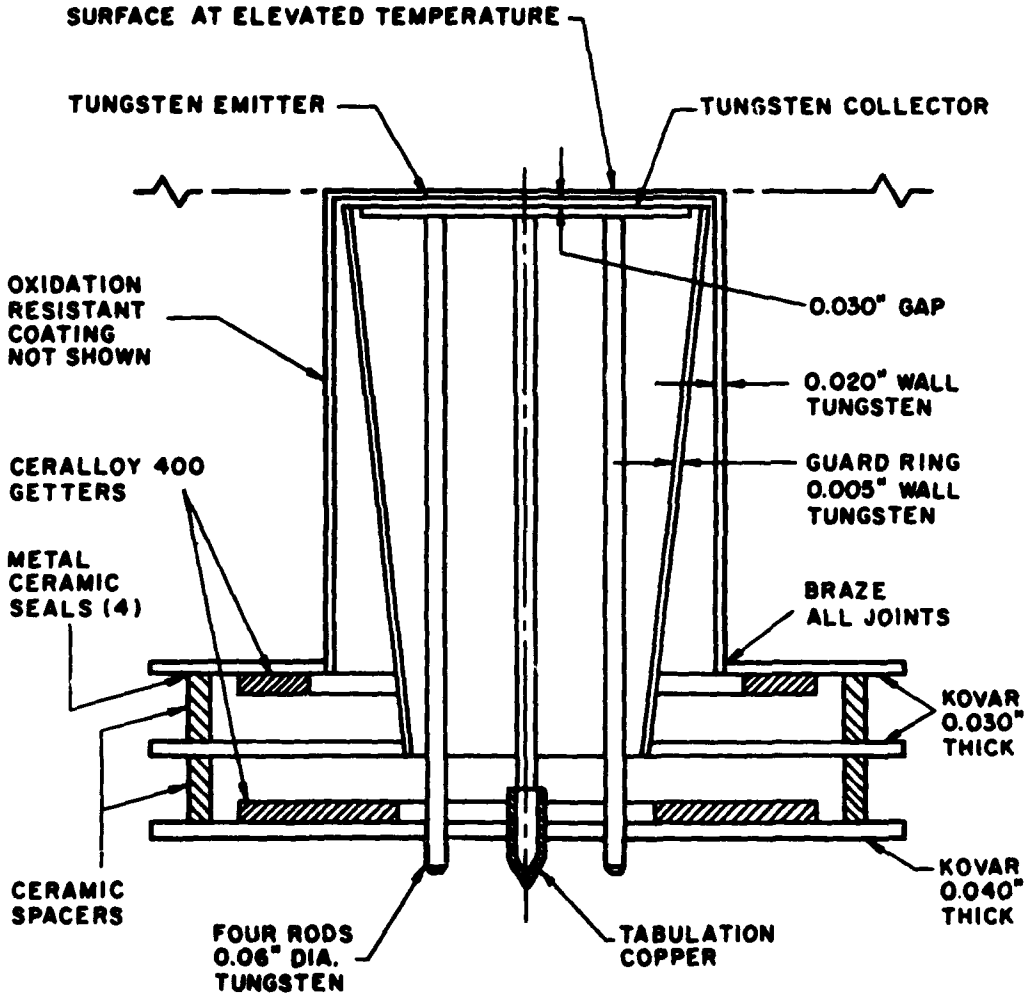

Figure 13. Surface Temperature Transducer

and the surface to be measured. A prime requisite for such a material is that it not migrate through the tungsten emitter. This may prove to be an impossible requirement at 2000°K, since even at lower temperatures migration of foreign metals through tungsten is a common phenomenon.

The major drawback to a thermionic surface-temperature transducer is the quantity of heat withdrawn from the surface by the transducer. The transducer has an outer envelope of tungsten or tantalum metal whose thermal conductivity is relatively high (about one-fourth to one-sixth that of copper at room temperature). Experience has shown that a thickness of 0.020 inches is necessary to ensure a leak-tight assembly at elevated temperatures. For the design shown, with an outside diameter of 4 centimeters, the cross-sectional area of the outer shell is 0.6 cm^2. For an estimated temperature drop of 500°C/cm, the heat flow through the outer shell will be approximately 500 watts by conduction alone. To this must be added heat conducted away by the shield and collector, and heat losses of this magnitude will seriously affect the surface temperature. Measurement of surface temperatures by thermionic means is thus not, in general, practical because of heat loss by conduction through the transducer.

4. DISCUSSION OF DESIGNS

Any one of the temperature transducers, including design No. 1, which is the most rugged of the three, will be extremely fragile (with the shock resistance of glass) even if constructed of some refractory metal other than tungsten, such as molybdenum or tantalum. The reason for this is that the transducers must be heated to a temperature well in excess of the recrystallization temperature and held there for hours to drive out entrapped gases. When the recrystallization temperature is exceeded, the structure of the metal changes, and relatively few large crystals are formed. The molecular forces holding one crystal to another are low, and when a strain is placed on the metal, there is slippage between the crystals, and failure results. Thus a transducer which may initially be constructed of a fine grained and tough material will, after being processed to enhance its thermionic properties, be weak and brittle at any temperature.

The gas temperature transducers, with their long cantilevered construction, will be extremely sensitive to vibration. Due to the large quantity of heat which is conducted along their length away from the emitter, they are suitable only for use in an environment with an excellent heat transfer coefficient from the gas to the transducer, such as in the exhaust nozzle of a jet or rocket where the gas velocities approach or exceed sonic velocities. Such environments are favorable to the production of vibrations, and components used therein should possess high vibration resistance, a quality the thermionic temperature transducers do not have.

Maintenance of a work function that is constant with time in the presence of temperature changes is most unlikely. Certainly the attainment of an accuracy of 1/2 of 1 percent in temperature indication is beyond the realm of possibility at present since such accuracies have not been obtained under the most rigid of laboratory conditions. Nottingham (Reference 2) states that the relationship between thermionic current and temperature is represented equally well by the theoretical relation,

$$I = A T^2 \epsilon^{\frac{-e\phi}{KT}}$$

or by the empirical one,

$$I = \alpha \epsilon^{-B/T}$$

due to scatter in the data. If the empirical equation is adjusted to give the same current as the theoretical equation at 1250° and 2500°K, the difference between the two currents will be equivalent to a temperature error of 0.5% at 1850°K, and slightly more at 1000° and 3000°K. The desired accuracies have never been attained under idealized laboratory conditions and cannot be expected in a practical instrument.

Bloomer (Reference 16) has obtained high accuracy and repeatable results using thermionic emission from a tungsten filament as an indication of temperature. He finds no evidence of poisoning above 2700°K but says it might be present at lower temperatures. All his tests were for temperatures in excess of 2750°K, which is far beyond the range of any corrosion-resistant coatings presently available.

The excellent results obtained by Magida (Reference 8) in maintaining the work function of a tungsten filament constant with time were obtained under very special conditions. The filament was operated at only one temperature. Consequently, a pseudostable condition may have occurred in which the tungsten surface was contaminated, but the degree of contamination did not change with time because all external parameters remained fixed. If such conditions could be obtained in a temperature transducer, there is a good possibility of obtaining a reasonably accurate device for operation above 2000° or 2200°K. Below this temperature, oxygen poisons an emitter even at pressures as low as 10^{-10} mm of mercury. Such pressures are attainable only with the most modern of ultrahigh-vacuum systems (Nottingham, Reference 2).

The pressure attainable in a temperature transducer will be no lower than that obtainable in a commercial vacuum tube, which is approximately 10^{-6} mm of mercury, and it will probably be much higher, since gases surrounding the transducer will diffuse through the emitter (which is the outer shell). At the high operating temperature of the emitter, the diffusion rate should be appreciable. The getter, which must be placed in the cooler parts of the transducer, will be less effective in removing the gases than it is in a vacuum tube because it is at the end of a long and narrow passage. It may be assumed that there will be carbon monoxide and nitrogen in the gases surrounding the transducer, and these will react with tungsten above 2200°K. It is anticipated that nitrogen will not poison the tungsten since the compounds will be evaporated as fast as they are formed. Good and Muller (Reference 5) state that carbon compounds will react with tungsten at temperatures as low as 1200°K, and that carbon compounds may be cleaned from the surface of tungsten by flashing at 2800°K. However, some of the carbon diffuses into the tungsten and will reappear

after operation at a lower temperature. We may therefore anticipate poisoning by carbon compounds in a temperature transducer used in the propulsion system of a vehicle.

Corrosion-resistant coatings start to fail rapidly at the temperatures at which a thermionic temperature transducer might be feasible, based on theoretical considerations. The best of the coatings have lifetimes of 12 to 16 hours at 3300° F (approximately 2100° K), which is the point at which a tungsten emitter would probably give reproducible results. However, it should be noted that the lifetimes given for the coatings are for mechanical failure of the substrate. A thermionic temperature transducer would probably fail long before a mechanical failure occurred because only a slight amount of gas diffusing through tungsten would spoil the high vacuum and poison the emitter. There is little possibility that any of the existing coatings would protect a thermionic temperature transducer above 2000° K.

Another adverse characteristic of the high-temperature coatings developed to date is their reduced lifetimes at temperatures of less than 1400° K. There is an inherent temperature gradient along a transducer since the emitter must operate at a high temperature while the metal ceramic seal is limited to a few hundred degrees Kelvin. Hence some portion of the transducer will be at a critical temperature below 1400° K with a lifetime of questionable duration.

SECTION VIII

CONCLUSIONS AND RECOMMENDATIONS

Tungsten would be the most satisfactory material to use as an emitter in a temperature transducer. It has the highest melting point of the metals and also has the highest strength at elevated temperatures. More experimental data have been collected on the thermionic properties of tungsten than on any other metal because its surface can be easily cleaned of impurities by flashing at 2800° K, and it is less susceptible to poisoning than other refractory metals. It is, however, poisoned by oxygen below 2000° K and will give repeatable results only if used above this range.

A thermionic temperature transducer will conduct large quantities of heat from the source whose temperature is being measured. It is suitable for use only in an environment where there is an excellent transfer of heat between the source and the transducer, such as in a gas stream approaching sonic velocities. The heat loss is inherent to the design since the emitter must operate at the temperature of the source while, because of structural limitations, the metal-ceramic seal between the emitter and collector cannot exceed several hundred degrees Kelvin. The cross-sectional area of the emitter and collector shell, along which the heat flows, is massive when compared to the area of a thermocouple wire. Consequently the transducer will be inferior to a thermocouple in its ability to register true source temperature for most applications.

Corrosion-resistant coatings for tungsten or any other refractory metal have a very limited life at temperatures above 2000° K. Very little testing has been done in other than atmospheric air at 1-atmosphere pressure, and the limited amount of testing that has been done in other environments indicates a reduced lifetime at low ambient pressures and at lower temperatures. The experience of others in obtaining a corrosion-resistant coating for use in a fossil-fuel gas environment has been poor. At the present time there is no evidence of a satisfactory long-life coating for use above 2000° K, which is the minimum temperature at which a tungsten emitter could be expected to produce repeatable temperature indications.

A thermionic temperature transducer is inherently a weak and fragile assembly. The refractory metals, including tungsten, must be heated to a temperature well above the recrystallization temperature to drive out sorbed gases. This renders the metal weak and brittle, with the shock resistance of glass, at both operating and room temperatures. Since the temperature transducer is a self-supported cantilevered device, it will be sensitive to vibration and cannot be considered a rugged instrument suitable for operational use in re-entry vehicles.

Summarizing the conclusions, it appears that it would be possible to demonstrate a relationship between thermionic current and temperature that would be repeatable above the temperature at which oxygen poisons tungsten, which is approximately 2000° K. However, the device would not be a temperature sensor in the usual sense of the word because it would have to operate in a high vacuum environment. Operation of a temperature transducer in a gas atmosphere

at temperatures above 2000°K would result in rapid deterioration of the corrosion resistant coating, permeation of the gas through the transducer, and a poisoned emitter.

It is recommended that Phase II of this project, fabrication of temperature sensors based on the designs developed, be dropped at this time since it simply demonstrates that the designed thermionic temperature transducers are not practical instruments, and the building of breadboard models would not advance the state of the art of high temperature measurement. At some future time with further development of long-life high-temperature coatings that are impervious to gas penetration, a thermionic temperature transducer may become feasible. If so, the project may be reactivated at that time.

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13. ABSTRACT

Several thermionic emission techniques were investigated for transduction of elevated temperature (i.e., above 2000 degrees Fahrenheit). Also several possible emitter materials and high temperature corrosion-resistant coatings were evaluated for three basic designs developed for prototype transducers. The range over which tungsten, the most satisfactory emitter material evaluated, could be expected to exhibit repeatable temperature indications exceeded the lifetime capabilities of the coatings. Since the designs developed were marginal as temperature transducers construction of models appeared to be an impractical means of demonstrating feasibility of the concept. State-of-the-art advancement obviously would not be achieved, therefore it was advisable to terminate the contract prior to model fabrication. The suitability of thermionic techniques for temperature transduction below 2000 degrees Fahrenheit was not considered in this program.

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